PB82-228917

Literature Review of Personal Air Monitors for Potential Use in Ambient Air Monitoring of Organic Compounds

Battelle Columbus Labs., OH

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Jun 82

U.S. Department of Commerce
National Technical Information Service
NTIS

EPA-600/4-82-048
June 1982

LITERATURE REVIEW OF PERSONAL AIR MONITORS FOR POTENTIAL USE IN AMBIENT AIR MONITORING OF ORGANIC COMPOUNDS

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to

U. S. Environmental Protection Agency

Contract # 68-02-2686

September, 1981

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

BIBLIOGRAPHIC INFORMATION

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PERFORMER: Battelle Columbus Labs., OH.
Contract EPA-68-02-2686

SPONSOR: Environmental Monitoring Systems Lab., Research Triangle Park, NC.
EPA-600/482-048

The open literature, Federal publications, industrial reports, and other sources published between 1975 and 1980 were reviewed for information relevant to personal air samplers potentially useful in sampling organic compounds at ambient levels (50-200 ppt). Seventy one references which identify fifty two groups involved in developing or marketing relevant instruments are cited. Four passive personal monitors and two active monitors developed for industrial hygiene levels are recommended for further testing and development for use at ambient levels. These monitors are DuPont's PRO-TEK G-AA; Abcor's GASBADGE; 3M's 3500 Organic Vapor Monitor; Real's Mini-Monitor; MDA's Accuhaler; and Bendix's BDX102. Laboratory tests are proposed in the areas of blank reduction/reproducibility, analytical methodology, and controlled atmosphere exposures. Following completion of laboratory tests, the most promising devices should be field tested to determine which monitors provide the most accurate and reliable data.

KEYWORDS: *Organic compounds, *Dosimeters, *Industrial hygiene, *Indoor air pollution, *Air pollution monitors, *Occupational safety and health.

Available from the National Technical Information Service, Springfield, Va. 22161

PRICE CODE: PC A05/MF A01

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise, and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

Human exposure to ambient levels of organic air pollution is an EPA objective which is currently limited in three areas:

1. Analytical techniques
2. Sampling methodology
3. Sampling instrumentation.

As part of the ongoing efforts of the Environmental Monitoring Systems Laboratory, this survey deals with the identification of instruments suitable for determining individual exposure to organic air pollutants. Knowledge of both the limitations and potential uses of existing instruments is a necessary EPA prerequisite for developing a cogent sampling strategy for individual exposure to organic air pollutants.

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ABSTRACT

The open literature, Federal publications, industrial reports, and other sources published between 1975 and 1980 were reviewed for information relevant to personal air samplers potentially useful in sampling organic compounds at ambient levels (50 - 200 ppt). Seventy one references which identify fifty two groups involved in developing or marketing relevant instruments are cited. Four passive personal monitors and two active monitors developed for industrial hygiene levels are recommended for further testing and development for use at ambient levels. These monitors are DuPont's PRO-TEK G-AA; Abcor's GASBADGE; 3M's 3500 Organic Vapor Monitor; Real's Mini-Monitor; MDA's Accuhaler; and Bendix's BDX102. Laboratory tests are proposed in the areas of blank reduction/reproducibility, analytical methodology, and controlled atmosphere exposures. Following completion of laboratory tests, the most promising devices should be field tested to determine which monitors provide the most accurate and reliable data.

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ACKNOWLEDGMENT

The assistance and technical guidance from the Task Officer responsible for this study, Mr. David O. Hinton, significantly contributed to the completeness and focus of this review. Helpful project discussions with Dr. Donald R. Scott of EMSL-RTP and Dr. Robert Coutant of Battelle are gratefully acknowledged.

SECTION 1

INTRODUCTION

It is important to obtain a data base that permits characterization of airborne contaminants encountered during daily activities to assure the health and safety of the general populace. Certain atmospheric hazards present in the industrial work place environment have been widely recognized and evaluated by a variety of monitoring methods. However, the general populace is exposed to different levels of organic pollutants and compounds which have not been monitored routinely. Further, the 24-hour ambient air exposure levels may be lower by one to three orders of magnitude than the industrial levels, i.e., 50-200 parts per trillion by volume (62). The disparity between lower ambient concentrations and high workplace levels provides the most difficult analytical problem for dosimeter applicability. Two recent publications cite data indicating that dosimeters may even be limited at low part per million threshold for some chemicals (17,25).

Personal monitoring of volatile environmental pollutants may be accomplished by using either passive devices, which do not require power, or active devices, which require a power source. Both types of monitors are designed to measure the concentration of a given substance in the air sampled. These personal monitors can then provide an indication of the ambient air level of the pollutant to which the individual is exposed.

The review of pertinent literature and government documents pertaining to personal air monitors presented in this report was restricted to monitors for measurement of organic compounds. Volatile halogenated hydrocarbons, benzene, and chlorobenzene were of particular interest since the Environmental Protection Agency is interested in determining personal exposure to organic compounds present in ambient air. The review was restricted to the period from 1975-1980 except for a few key 1981 references. The objective of the literature survey was to recommend the most likely candidates for further evaluation and development.

PASSIVE PERSONAL MONITORS

Passive personal monitors generally measure time weighted average (TWA) concentrations of compounds by using the principles of diffusion and/or permeation. Devices which operate by diffusion are designed so that gas molecules pass through a stagnant layer of air and are collected on an adsorbent such as charcoal. Turbulence is minimized by using draft shields or tubes and holes which have a length to diameter ratio of greater than three. The permeation process occurs when gas molecules come into contact with a solid membrane. The molecules dissolve, diffuse through the barrier, and are collected on a sorbent material.

ACTIVE PERSONAL MONITORS

Active personal monitors require the sustained performance of a precision pump to deliver a continuous flow of air at a known rate to a collector which is usually an adsorbent material such as activated charcoal or silica gel. Subsequent analysis of the adsorbent material provides data for the total mass of contaminant present in the known volume of air sampled so that ambient concentrations can be determined.

From 1975 through 1980, research and development on the production of passive and active personal monitors has experienced a rapid growth. This review of the state of the art for personal air monitors has identified 52 groups involved in the development of this technology over this 5-year time period. Information has been evaluated for this review to identify pollutant monitors that may be applicable for 24-hour personal ambient air monitoring and also to recommend areas where research and development are needed.

MONITOR SELECTION

Selection and ranking of candidate monitors for testing and further development is based on several assumptions:

- Impingers are inappropriate due to complications introduced when handling liquids (logistics). Detection limit technical problems due to dilution are magnified since ambient air concentration levels are lower than workplace concentrations.
- Breakthrough due to saturation of adsorbents such as charcoal is normally not a limiting factor for ambient air monitoring due to relatively lower pollutant concentrations.
- Battery systems which are generally adequate for 8-hour sampling are insufficient for ambient air (24-hour) monitoring.
- The capability to obtain average concentrations of organic compound over 24 hours is essential and to obtain the peak concentration during the sampling period is a desirable feature.
- The passive monitors should collect sufficient concentrations of the compounds of interest through passive gradient diffusion to the active colleciton surface to be both detectable and to exceed the background concentrations of these compounds in the collection media.

SECTION II

CONCLUSIONS

A variety of methods were reported for sampling and analysis of organic vapors in air from 1975-1980. Most of these methods tested the applicability of an adsorbent for either specificity or versatility for sampling several organic constituents in air. The most common adsorbents studied were activated charcoal and silica gel with several uses reported for XAD-2, Chromosorb 100 series, Tenax-GC and Porapak. Only a few methods employed liquid impingers. The analytical technique most frequently used was gas chromatography and some methods required analysis by high performance liquid chromatography and colorimetric methods.

Application of these methods for developing commercially available personal monitors has resulted in marketing of seven dosimeters:

1. GASBADGE (Abcor)
2. Model 3500 Organic Vapor Monitor (3M)
3. PRO-TEK G-AA (DuPont)
4. PRO-TEK G-BB (DuPont)
5. MINI-MONITOR (REAL, Inc.)
6. Accuhaler (MDA)
7. BDX102 (Bendix)

These devices are currently marketed for monitoring air in the workplace, but several units show promise for ambient air monitoring. The most common disadvantage of the workplace monitors, saturation of the adsorbent collector with organic vapor, should not be a problem for ambient air monitoring since the organic compounds are present at significantly lower levels (50-200 ppt by volume) (62). For example, the GASBADGE is recommended for maximum exposure of 500 ppm-hours. At ambient concentration levels of 50 ppt, the 8-hour recommended maximum sampling time may theoretically be extended to a year.

One of the anticipated limitations for applying either active or passive personal ambient monitoring is high blanks coupled with low total exposures. For example, the mass of organic collected by the DuPont PRO-TEK badge in 24 hours is calculated (using a background of 50 to 200 parts per trillion) to be 30 ng to 130 ng. The blank requirement, assuming a maximum of 10 percent of collected mass of 3 to 13 ng, is very low because some devices show 10 to 1000 ng blank values for organic compounds (12). The total exposure of 0.001-0.005 ppm-hours is significantly lower than specifications listed by commercial suppliers.

Further research is needed in four areas:

1. Blank reduction and reproducibility
2. Analytical methodology to reliably extract and detect compounds at anticipated levels
3. Chamber exposure tests
4. Field testing if laboratory tests are promising.

Those monitors recommended for laboratory and field testing on the basis of flow rate, size, cost, and operational considerations include the passive monitors:

- PRO-TEK G-AA (DuPont)
- GASBADGE (Abcor, National Mine Service Company)
- Model 3500 Organic Vapor Monitor (3M)
- MINI-MONITOR (REAL, Inc.)

and the active monitors:

- Accuhaler (MDA)
- BDX102 (Bendix).

Passive

The DuPont PRO-TEK badge, the G-AA, is recommended to test accuracy of sampling during variable air flows. Since saturation of the collector is not anticipated, the G-BB with a special backup collection feature does not appear to be necessary. A permeation device should be extensively tested in the laboratory to determine if any advantages are realized over the other devices. The MINI-MONITOR has been field tested for vinyl chloride, and this device is recommended for laboratory testing, but each badge must be individually calibrated for each pollutant. Insufficient data are available for concluding whether the Porton Diffusion Sampler is suitable for laboratory and field use.

Active

The commercially available active personal monitors include a variety of pumps and associated collection tubes, usually charcoal, for organic vapor sampling and analysis. These pump based systems usually provide flow rate accuracies of five to ten percent. Selection of active devices for field testing under ambient air conditions is difficult since the pump/charcoal tube systems are very similar in design (size, weight) and operating parameters (air sampling rate, accuracy).

The costs of active samplers are generally higher (average estimated at $400) than passive monitors ($5-25), with the exception of the permeation device, which costs $100. The devices recommended for laboratory and field testing were selected to offer some variation in design or operation with

preference given to those units field tested most extensively in the workplace. The MDA Accuhaler shows promise since an adjustable air sampling rate is feasible and several adsorbents have been tested. The Bendix BDX102 also is suggested for laboratory evaluation and field testing to cover higher air sampling rates. The MDA Chronotox is not recommended since the high cost ($10K) would be prohibitive and it is used primarily for inorganic compounds.

More useful information may be provided if the MDA and Bendix pumps are evaluated using several adsorbents and some combinations of adsorbents rather than by examining additional pump systems. Liquid impingers involve logistical inconveniences not encountered using solid adsorbents so further evaluations of impingers is not considered beneficial.

A prototype miniature gas chromatograph has been developed at Stanford Research Institute. Although portable, it is not considered a personal instrument. For purposes of this report, it does not warrant further development recommendations as further improvements in specificity, further miniaturization, and reduced power requirements are required. It does represent a major step in size/weight reduction for gas chromatographs, therefore its progress should be followed.

SECTION III

RECOMMENDATIONS

1. None of the personal monitors currently available commercially have been extensively tested under ambient air conditions. Some limited laboratory evaluation of commercially available passive devices has been completed (12). Only those devices which show promise for ambient applications should be evaluated in the laboratory and field tested within a range of typical ambient related humidities and temperatures.

2. The four passive personal monitors recommended for this evaluation are:

- PRO-TEK G-AA (DuPont)
- GASBADGE (Abcor-National Mine Service Company)
- Organic Vapor Monitor 3500 (3M)
- MINI-MONITOR (REAL, Inc.).

a. It is recommended that these three diffusion units and the permeation device be extensively tested in the laboratory and field. The laboratory tests proposed include three areas:

- Blank reduction and reproducibility--currently available badges show blank values from 10 to 100 ng for certain compounds (12).
- Analytical methodology--the low ambient air organic concentrations (ppt levels) indicate the need to develop and validate applicable extraction and detection methods.
- Chamber exposure tests--the badges which meet analytical specifications (low blank, reliable analysis technique) should be exposed in controlled atmospheres containing concentrations of organic compounds typical for ambient conditions.

b. Following completion of laboratory evaluation, field tests are proposed to determine which diffusion monitors provide the most accurate and reliable data, and whether the permeation device offers any advantage or has shortcomings. The Organic Vapor Monitor 3500 (3M) and GASBADGE (Abcor National Mine Service Company) have been most extensively evaluated and should be a part of the evaluation study. A third diffusion device,

PRO-TEK G-AA manufactured by DuPont shows the most promise for field testing. The MINI-MONITOR (REAL, Inc.) is currently available only for vinyl chloride monitoring. Extension of applicability of this permeation device to other organic compounds may be less straightforward than for the diffusion controlled units. Laboratory and field testing in parallel with the other three devices should provide preliminary information required to assess potential for ambient air monitoring, however, examination of more than one membrane (dimethyl silicone and silicone polycarbonate) is recommended. Activated charcoal should be used to eliminate any variations in efficiency and accuracy introduced from variations of adsorbent material because charcoal is used for all four diffusion devices recommended for field testing.

3. Two active personal monitors recommended for field testing are:

- MDA's Accuhaler
- Bendix BDX102 Sampler.

These systems offer a broad range of sampling rates and provide comparable operating reliability. Numerous pump-adsorbent combinations are on the market, so preference was given to those devices already tested as personal monitors.

4. Following laboratory field testing of the six monitors recommended, it should be possible to define developmental needs required for accurate personal monitoring in ambient air conditions. Optimization of adsorbent efficiency by using a combination of materials such as silica gel and charcoal is a possible area requiring research support. The specific operating parameters such as sampling rate and adsorbent configuration may also require adjustment and modification. The criteria for evaluation of air sampling methods for solid sorbents developed by Melcher et al will be used to define minimum acceptability of the methods studied (42). Included in these evaluations are effects of humidity, storage, temperature, coadsorption, and blank levels.

5. There is a deficiency of information regarding precision and accuracy for all of the commercial active and passive monitors discussed in this review. A detailed analytical study for the one or two devices shown to be most promising for ambient air monitoring to establish precision, sensitivity, and accuracy is recommended. Interferences from environmental conditions (humidity, temperature, corrosive atmosphere) and chemical constituents should also be carefully examined and clearly stated.

SECTION IV

APPROACH

This survey of the state of the art for personal air monitoring was conducted by reviewing technical publications in key journals, and by contacting researchers in the Federal, academic, and industrial sectors. The most pertinent published sources included:

- American Industrial Hygiene Association Journal
- Annals of Occupational Hygiene
- Chemical Abstracts Section 59, Air Pollution and Industrial Hygiene
- Industrial Hygiene Digest
- Industrial Hygiene News Report.
- Evaluation of Ambient Air Quality by Personnel Monitoring (39).

The review was limited to articles published from 1975-1980, except for a few 1981 references.

Personal contacts and published promotional literature from industrial firms active in the field provided data for commercially available passive and active monitors. The companies and universities engaged in personal monitor research identified for this review are listed in Appendix A.

The review of available data generated information which may be classified in five major measurement method areas:

- Organic vapor sampling and analysis
- Passive personal monitors
- Active personal monitors
- Collection media
- Miniature gas chromatograph.

Detailed descriptions of these subjects including abstracts of pertinent technical publications are presented in Appendix B arranged under the above five headings. Each section of Appendix B is presented in a format such that each area may be consulted separately, or the five areas may be read as a unit separate from the body of this report. The specific arrangement for each section is described at the beginning of that section.

References and personal contacts consulted for this review are presented in the Bibliography in alphabetical order. The references are numbered so that articles can be cited in a consistent manner both in Appendix B and in the body of this report.

Section 1 deals with organic vapor sampling and analysis and presents information describing development of methods for specific organic compounds. The majority of these methods include collection of vapor on an adsorbent, most commonly activated charcoal or silica gel, and analysis of the adsorbent by gas chromatography. Key elements of the methods identified from the review of the open literature from 1975-1980 are summarized in Table 1, and a detailed discussion of each method is presented in Section 1 of Appendix B.

Additionally, available technical background information used in the developmental or evaluation phases for both passive and active devices is provided in Section 1 of Appendix B. Discussions, presented in Sections 2 and 3 and Appendix B for passive and active personal monitors, respectively, include descriptions of commercially available devices.

To distinguish between passive and active devices, the following criteria were used:

Passive:

Requires no power source
Weighs less than 50 grams
Uses diffusion or permeation for air sampling
Contains a collector for organic compounds.

Active:

Operates for a minimum of 8 hours without recharging batteries
Weighs less than 2500 grams
Samples air at a minimum flow rate of 50 ml/min
May be comfortably worn for a minimum of 8 hours
Contains a collection device for organic compounds.

Section 4 deals with impingers or adsorbent evaluation. Section 5 describes the development of a miniaturized gas chromatograph since this technology may be important to this research area.

TABLE 1. SUMMARY OF METHODS FOR ORGANIC VAPOR COLLECTION AND ANALYSIS WITH ACTIVE AND PASSIVE DEVICES

Target Organic Constituents	Adsorbent	Analysis Procedure	Reference
Acrolein	Hydroquinone-treated carbon	Gas chromatography	30
Acrylates	Activated silica gel	Gas chromatography	5
Amines	Silica gel	Ion chromatography	4
Anilines	Silica gel	Gas chromatography	69
Benzidines	Silica gel	High performance liquid chromatography	44
Carbon disulfide	Charcoal	Gas chromatography	41
Chlorinated isocyanuric acids	Polyvinyl chloride-copolymer membrane	Potentiometry	54
Cyclopentadiene	Chromosorb 104 coated with maleic anhydride	Gas chromatography	18
Diazomethane	XAD-2 coated with octanoic acid	Gas chromatography	22
Dinitrotoluene	Silica gel	Gas chromatography	29
Ethylene oxide	1. Liquid (H_2SO_4) impinger 2. Activated carbon	1. Gas chromatography 2. Gas chromatography	56 55
Furfural	Impinger (Gerard T reagent)	High performance liquid chromatography	21
Hydrazine	Sulfuric acid coated silica gel	Gas chromatography	11
Hydrocarbons and Common Organic Solvents:			
1. Hexachlorobutadiene	1. Amberlite XAD-2	1. Gas chromatography	15
2. Hexachloro-cyclopentadiene	2. Porapak T	2. Gas chromatography	15
3. 1,2-dichloropropane	3. Petroleum charcoal	3. Gas chromatography	15
4. Aliphatic hydrocarbon	4. Silica gel	4. Gas chromatography	7
5. Variable volatility/ polarity	5. Tenax GC-Porapak R-Ambersorb combination	5. Glass capillary gas chromatography	6
6. Hydrocarbons	6. Activated charcoal	6. Gas chromatography	24
7. Polar/nonpolar solvents	7. Activated charcoal	7. Gas chromatography	36
8. Toluene	8. Gas detector tubes	8. Stain length	27
9. Aliphatic and aromatic hydrocarbons; ketones	9. Chromosorb 101	9. Thermal desorption; gas chromatography	50
10. Chlorinated alkanes and alkenes; solvents	10. Tenax GC; Porapak N	10. Thermal desorption; gas chromatography and GC/MS	13
Mercaptans	Mercuric acetate treated glass wool plug	Colorimetric	46
Methyl isocyanate	XAD-2	High performance liquid chromatography	65
Nitrosoamines	Chromosorb 101-108 Tenax-GC	Gas chromatography	31
Organic bases (hydrazines and amines)	Activated silica gel	Gas chromatography	70
Organic sulfates (diethyl/dimethyl)	Silica gel	Gas chromatography	19
Organometallics:			
1. Organotins	1. Glass fiber filter	Flameless atomic absorption spectrophotometry	28
2. Lead alkyls	2. Porapak Q	Flame atomic absorption spectrophotometry	10
Organophosphates	XAD-2	Gas chromatography	33
Phosgene	Treated filter paper	Colorimetric	14
β-propiolactone	Treated cellulose thin layer chromatography strips	Ultraviolet fluorescence	58
Thiourea	Midget impinger with water	Colorimetric	53
Vinyl chloride	1. Dimethyl silicone membrane over activated charcoal	1. Gas chromatography	47, 66, 67
	2. Activated charcoal	2. Gas chromatography	35, 45

SECTION V

RESULTS AND DISCUSSION

PASSIVE PERSONAL MONITORS

Although none of the commercially available monitors were designed for ambient applications, seven passive workplace monitors are commercially available which employ either diffusion or permeation to sample air. Other companies have passive monitors under development including Galson Technical Services, Inc. (chlorinated organics) (51c) and Mine Safety Appliances Company (51c,51d). The seven passive personal monitors identified for this literature evaluation include four types of devices which operate using diffusion for air sampling.

- GASBADGE was developed by Abcor and is currently marketed by National Mine Service Company (51a). This dosimeter has an orifice in the front of the cover which permits diffusion of the contaminant and adsorption on the activated charcoal collection element (64). Analysis of the collection element after exposure provides the time weighted average (TWA) concentration of the contaminant of interest. The GASBADGE is applicable for monitoring a number of air pollutants. Several validation studies performed for the GASBADGE report reproducible monitoring data (3,61).
- Model 3500 Organic Vapor Monitor was developed by and is manufactured by 3M (20,51b). This dosimeter uses a charcoal pad located inside the monitor separated from a diffusion membrane by spacers. The TWA exposure of the wearer to contaminants collected on the absorbent pad is provided. This badge was tested for ability to monitor exposure to haloethanes in hospital operating rooms (40). A number of studies conducted to compare the GASBADGE and Model 3500 Organic Vapor Monitor reported that both dosimeters perform as reliable indicators of exposure to organic vapors (8,40,71). Both badges were also evaluated in parallel with active personal monitors (pumps and charcoal tubes) confirming earlier studies which claimed no statistical differences for passive sampler data and pump/charcoal tube data for industrial hygiene concentration (ppm) (63).

- DuPont's PRO-TEK series (G-AA and G-BB) use charcoal strips to collect organic vapors through the mechanism of molecular diffusion. The G-AA dosimeter samples air at the rate of 50 ml/min with one cover removed or 100 ml/min with both covers removed. The G-BB badge with backup is recommended for sampling compounds with high vapor pressure or when humidity and/or pressure are high. Analysis of the backup section is useful to indicate if saturation of the first section has occurred or to extend the sampling time.

- A commercially available dosimeter for vinyl chloride, the MINI-MONITOR, employing permeation sampling is marketed by REAL, Inc. (48). The MINI-MONITOR, developed by West, et al (47,66,67) is comprised of a permeable dimethyl silicone membrane and an activated charcoal collector. Applications for monitoring Freon and methyl chloride are under development (51e).

A personal dosimeter developed by MDA specifically for monitoring phosgene also employs the principle of molecular diffusion for sampling. The collection and analysis function is performed using a tape consisting of proprietary material which develops a stain proportional to exposed phosgene concentration. This device is probably based on the method by Diller, et al which uses a strip of filter paper impregnated with 4-(4'-nitrobenzyl)-pyridine and N-phenylbenzylamine (14).

Two companies, Moleculon and Monsanto Research, are developing devices for use as passive personal monitors, but these devices are not commercially available. Moleculon is using a microporous, homogeneous membrane called Poroplastic for monitoring exposure to ammonia (49). Monsanto Research Corporation has developed prototype dosimeters using Porapaks N and R to monitor organic vapors such as benzene, acrylonitrile, hexane, vinyl acetate, toluene, and vinylidene chloride (52).

The British Chemical Defense Establishment developed the Porton Sampler which operates using both the diffusion and permeation principles (1). The sampler consists of a gas permeable plastic membrane backed by a charcoal-cloth adsorbing disk mounted in a plastic holder similar to the radiation film badge design. Two membranes, silicone rubber and porous polypropylene, were found to be suitable. The charcoal cloth adsorbent medium was efficient for collection of organic compounds with boiling points at or near room temperature.

The pertinent specifications (size, weight, cost, exposure, range, air sampling rate, accuracy) are summarized for the commercially available passive personal monitors in Table 2. The tested applications for the passive personal monitors are also listed in Table 2 followed by advantages and disadvantages of each system and recommendations for ambient air applicability. Detailed descriptions of these passive monitors and comparable research studies are provided in Section 2 of Appendix B.

TABLE 2. PASSIVE AIR MONITORS

Device	Manufacturer	Dimensions, cm	Weight, g	Cost, $	Range for Exposure, ppm-hrs	Estimated Air Sampling Rate, ml/min	Accuracy, percent
GASBADGE	Abcor (National Mine Service Company)	5.1 x 6.5 x 1.6	28	10	0.5-500	30-45	25
Model 3500 Organic Vapor Monitor	3M	8.9 x 4.4 x 1.3	12	6	30-3000	30	25
PRO-TEK G-AA	DuPont	7.1 x 0.8 x 1.3	8	5	0.2-2000	50-100	25
PRO-TEK G-BB	DuPont	7.7 x 0.9 x 1.6	11	8	0.4-8000	50-100	25
Gas Monitoring Dosimeter (GMD)	MDA	5.7 x 3.8 x 0.8	7	2	0.01-5	30-50	200
MINI-MONITOR	REAL	Circular 5 cm diameter 0.6 cm thick	35	100	0-5	30-50	25
Porton Diffusion	British Chemical Defense Establishment	Circular (4 cm^2 exposed area)	Not available		Not available		Not available

(a) Specifications are estimates.

Tested Applications	Advantages	Disadvantages	Recommendations
Ethyl acetate, styrene methyl ethyl ketone, benzene, acrylonitrile SO_2 NO_2 methyl isobutyl ketone, isooctane, butyl acetate, methyl chloroform, tri-chloroethylene, butanol	• Calibration data available for organic compounds of toxicological importance • Lightweight and inexpensive	• Not suitable for ethylene oxide, methyl amines, formaldehyde, isocyanates, methane, ethane, propane • Monitoring of ambient air will involve competition between organics for adsorption	Application for ambient air personel monitoring likely - laboratory and field testing needed to define development needs
Ketones, nitriles, esters, alcohols diolefins, amides aliphatic and aromatic hydrocarbons, Freons, aldehydes, chloronated aliphatic hydrocarbons	• Comparable low cost and • Extension to cover other organic constituents likely	High humidity alters adsorption of some organic compounds.	Laboratory and field testing appropriate to define developmental needs for ambient air applications
Various organic vapors	• Variable sampling rates possible • Low range for exposure	None	Laboratory and field testing to define developmental needs for ambient air applications most promising dosimeter
Compounds with high vapor pressure (vinyl chloride, methylene chloride, acetone, Freon, pentane)	• Back-up charcoal device would indicate break-through from primary charcoal collector • May be used in high temperature (>32C) and high humidity (>80%) atmosphere	Limited applicability; for high pressure compounds	Not recommended for further testing since G-AA more universal with variable sampling rates
Phosgene	No separate detection analysis required	• Useful only for phosgene • Narrow exposure range	Not suitable for ambient air monitoring
Vinyl chloride	• No effect from humidity • Linear from 5ppb to 50ppm	• More expensive than other units described • Must be calibrated separatelv for each pollutant	Laboratory and field testing to determine if membrane permeable device has advantages for ambient air monitoring over diffusion type
Carbon tetrachloride, styrene, Freon, methyl ethyl ketone	Non-specific	Limited range of compounds - effective for compounds boiling from -30 to 145°C	Insufficient data to evaluate

ACTIVE PERSONAL MONITORS

Active personal monitors, summarized in Table 3, are commercially available from several sources including:

- Bendix Corporation
- Daco Products, Inc.
- EI DuPont de Nemours and Co. (Inc.)
- Environmental Measurements
- Matheson Gas Products
- MDA Scientific, Inc.
- Mine Safety Appliance Co.
- National Draeger, Inc.
- Sipin Company, Inc.

The Bendix Corporation has developed a series of BDX pumps using both charcoal tubes and midget impingers for air monitoring of organic vapors. The BDX55 HD pump was designed to sample coke emissions with impingers while the BDX34 LF sampler uses standard charcoal. The BDX102 offers two sampling rates and tested applications for a number of toxicologically important organic compounds. The BDX60 Super Sampler is similar to the BDX55 HD pump and neither offer air sampling rates less than 1000 ml/min.

Daco Products, Incorporated, markets the P0301 and P0304 pumps designed to sample through charcoal tubes or impingers using either nickel-cadmium or lead acid batteries. Daco also offers the Diff Sampler which uses only liquids to collect constituents from air. DuPont offers pumps suitable for collection of vapors and particulates using a variety of collection devices including charcoal tubes, liquid impingers, cyclones, and particulate filters.

The Pulse Pump III is available from Environmental Measurements, Inc. and is recommended for personal monitoring for exposure to hydrocarbons and a number of inorganic pollutants. The highest sampling rate possible with this pump is 330 ml/min.

MDA Scientific, Inc., markets the Accuhaler pump designed for use with several adsorbents including charcoal tubes, silica gel, and length-of-stain chemical tubes. A variety of limiting orifices and two sampling rate ranges are available. The Accuhaler costs from $330-430 depending on the number of orifices selected and the battery system of choice. The Model 4000 Miniature Continuous Monitor equipped with a Model 4100 Integrating Reader aspirates air through a moving chemically impregnated tape producing a stain with intensity proportional to the concentration of pollutant. Tested applications include phosgene and diisocyanate.

A microprocessor controlled personal monitor (Chronotox) is also manufactured by MDA (34). The Chronotox provides hard copy data for chemical concentration versus 90-second data points and an 8-hour threshold limit value. When programmed permissible levels are exceeded, the Chronotox records the duration of the event and the value representing peak exposure. The cost of the system is $10,000.

TABLE 3. ACTIVE PERSONAL MONITORS

Device	Manufacturer	Dimensions, cm	Weight, g	Cost, $	Estimated Air Sampling Rate, ml/min	Accuracy, percent	Tested A
BDX55HD	Bendix	11.9 x 12.7 x 6.5	850	400	1000-3000	±5	Coke oven em personal moni aromatic isoc
BDX34LF	Bendix	11.9 x 10.2 x 6.5	620	410	25-200	±5	Monitoring or with charcoal
BDX102	Bendix	31.8 x 28.6 x 11.4	2150	725	25-200 1000-3000	±5	Dusts and ace carbon tetrac chloroform, m ketone, tolue ethylene, vin
BDX60 Super Sampler	Bendix	11.9 x 12.7 x 6.5	840	400	1000-3000	±5	Vapors, hazar particulate m
PO 301 & PO 304	Daco	7 x 12.4 x 3.8	200 530	85 160	5-1000	±10	None given
P30A, P125A, P200A P2500 P4000	DuPont	3.8 x 7.5 x 13.3 8.3 x 10.2 x 16.5 6.7 x 10.2 x 15.2	14 26 34	550 495 895	10-4000	±5 ±5 ±5	Collectors su tubes, imping particulate f
Pulse Pump III	Environmental	4.1 x 7.4 x 10.2	225	145	15-330	±10	Freon, carbon hydrocarbons, carbonyl sulfi
Accuhaler	MDA	13.2 x 6.4 x 3.2	390	330-430	0.5-100 1-25	±10	None given
Miniature Continuous Monitor (MCM)	MDA	15.2 x 5.7 x 10.2	680	Not given	100	±10	Toluene diisocy
Chronotox	MDA	(pocket size)	1250	10000	100	±10	Organic diisocy toluene, toluen aromatic amines
C-210 Pump	MSA	12.7 x 6.4 x 3.2	170	375	5-20 5-200	±10	Organic vapor, carbon dioxide, monoxide, HCN
SP-15 and Sipin-Kitawaga Multiple Gas Dosimeter	Sipin	3.2 x 6.4 x 13	311	470	2-200	±5	Personal monito solvents

racy, ent	Tested Applications	Advantages	Disadvantages	Recommendations
	Coke oven emissions monitoring, personal monitoring for aromatic isocyanates	None	Flow rate of 50 ml/min not possible	Not recommended due to 50 ml/min flow rate available in more applicable unit
5	Monitoring organic vapors with charcoal adsorbent	None		Not recommended since no advantages over more tested devices (BDX102)
3	Dusts and acetone, benzene, carbon tetrachloride, chloroform, methyl butyl ketone, toluene, trichloro-ethylene, vinyl chloride	• Two flow rates possible • Tested for personal monitoring	Larger and heavier	Laboratory and field test to determine applicability for ambient air monitoring
3	Vapors, hazardous gases, particulate matter	Usable for continuous sampling	Flow rate of 50 ml/min not possible	Not recommended since no advantage over BDX102
0	None given	Useful with impingers and charcoal tubes		Not recommended for field testing--similar to Bendix units
5 5 5	Collectors such as charcoal tubes, impingers, cyclones, & particulate filters tested	Accurate flow rate (±5%) for all collector devices		
0	Freon, carbon dioxide, total hydrocarbons, carbon monoxide, carbonyl sulfide, mercaptans	None		
0	None given	• Current model able to sample 40 hr at 10 ml/min • Designed for use with several adsorbents including charcoal, silica gel, length-of-stain chemical tubes		Laboratory and field test to determine applicability for ambient air monitoring
0	Toluene diisocyanate, phosgene	Integrator/recorder to read exposure level available	Moving tape developed for few compounds; limited range (0-0.08 ppm toluene diisocyanate)	Not suitable for ambient air monitoring
0	Organic diisocyanates, dinitro-toluene, toluene diamine, aromatic amines, HCl, ammonia	Averages readings every 90 seconds and provides concentration vs time profiles over 12 hours--could be easily programmed for 24 hr	• Microprocessor & display equipment is expensive ($7K of $10K price) • Individual detectors required for each compound	Obtain more information but not promising for general organic sampling
0	Organic vapor, aromatic amines, carbon dioxide, carbon monoxide, HCN	Variety of applicable collection devices		
5	Personal monitoring of organic solvents	• Solvents other than activated charcoal being developed • Dual dosimeter fusion	Length-of-stain tubes compound specific	Not recommended, however, dual sample feature interesting

Mine Safety Appliances Company markets the C-210 pump designed primarily as a personal sampling pump powered by nickel-cadmium batteries. Charcoal and silica gel tubes are available for sample collection. National Draeger, Inc., offers the Polymeter, a combination of a personal monitoring pump, specific detector tubes, and a quantifying unit (quantimeter), for $2,000. The system samples at a maximum rate of 15 ml/min which is too slow for ambient conditions.

Under NIOSH sponsorship, Sipin Company developed a personal monitor commercially available as the Model SP-15. Tubes of standard NIOSH activated charcoal are used and additional absorbent materials are being tested by Sipin. This company also markets the Sipin-Kitawage Multiple Gas Dosimeter which uses the SP-15 pump and length-of-stain dosimeter tubes. A dual gas adapter permits samples to be drawn simultaneously through two adsorbent tubes.

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APPENDIX A

SOURCES OF SUBJECT TECHNICAL CONTACTS

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SOURCES OF SUBJECT TECHNICAL CONTACTS

Groups involved in research or commercial development of personal air monitors:

Abcor, Incorporated
Walden Division
Wilmington, Massachusetts 01887

Allied Chemical Corporation
Chemical Division
Buffalo, New York 14210

Arthur D. Little, Incorporated
Acorn Park
Cambridge, Massachusetts 02140

Bayer, A. G.
Sverkusen-Verdingen
F. R. Germany

Becton, Dickinson, and Company
Energetics Science Division
Elmsford, New York 10523

Bendix Corporation
Environmental and Process Instruments Division
Lewisburg, West Virginia 24901

British Chemical Defense Establishment
Porton Down
Salisburg
Wiltshire, England

CEA Instruments, Incorporated
15 Charles Street
Wentwood, New Jersey 07675

Colorado State University
Fort Collins, Colorado 80523

Daco Products, Incorporated
12 South Mountain Avenue
Montclair, New Jersey 07042

Dow Chemical, U.S.A.
Midland, Michigan 48640

Dow Badische Compnay
Williamsburg, Virginia 23185

E. I, Du Pont de Nemours and Company
Applied Technology Division
Wilmington, Delaware 19898

Environmental Measurements, Inc.
1037 North Fair Oaks Avenue
Sunnyvale, California 94056

Epply Institute
Cancer Research
University of Nebraska
Omaha, Nebraska 68105

Esso Europe, Incorporated
Esso Research Center
Abingdon, Oxon, England

Ethicon, Incorporated
Somerville, New Jersey 08876

Galson Technical Services, Inc.
East Syracuse, New York 13057

General Electric Company
DECP/AIESD
50 Fordham Road
Wilmington, Massachusetts 01887

Giangarlo Scientific Company
3237 Dawson Street
Pittsburgh, Pennsylvania 15213

Harvard School of Public Health
Department of Environmental Sciences
665 Huntington Avenue
Boston, Massachusetts 03115

H-NU System, Incorporated
30 Ossipee Road
Newton, Massachusetts 02144

Industrial Analytical Laboratories
1523 Kalakanka Avenue
Honolulu, Hawaii 96826

John Hopkins University
Baltimore, Maryland 21205

LFE
Environmental Analysis Laboratories
2030 Wright Avenue
Richmond, California 94804

Los Alamos Scientific Laboratory
Los Alamos, New Mexico 87545

Louisiana State University
Environmental Sciences Institute
Baton Rouge, Lousiana 70803

3M
Occupational Health and Safety
Products Division
St. Paul, Minnesota 55133

Matheson Gas Products
Lyndhurst, New Jersey 07071

MDA Scientific, Incorporated
1815 Elmdale Avenue
Glenview, Illinois 60025

Mine Safety Appliances Company
600 Penn Center Boulevard
Pittsburgh, Pennsylvania 15235

Moleculon Research Corporation
130 Main Street
Cambridge, Massachusetts 43021

Monsanto Research Corporation
Dayton, Ohio 45407

National Draeger, Incorporated
401 Parkway View Drive
Pittsburgh, Pennsylvania 15205

National Institute for Occupational
Safety and Health
U. S. Department of Health, Education
and Welfare
Public Health Service
Cincinnati, Ohio 45202 or 45226

National Mine Service Company
Safety Systems and Products
U. S. Rt. 22 and 30 West
Oakdale, Pennsylvania 15071

New York University Medical Center
Institute of Environmental Medicine
550 First Avenue
New York, N. Y. 10016

Occupational Medicine and Hygiene
Laboratories
Health and Safety Executive
London, England

Radian Corporation
Austin, Texas 78712

Reiszner Environmental and Analytical
Laboratories (REAL)
P. O. Box 3341
Baton Rouge, Louisiana 70821

Rockwell International
5529 Chapel Hill Boulevard
Durham, North Carolina 27707

Rohm and Haas Company
Laboratory 65
Briston, Pennsylvania 19007

Anatole J. Sipin Company, Incorporated
505 Eighth Avenue
New York, N. Y. 10018

Southwest Research Institute
P. O. Drawer 28510
San Antonio, Texas 78284

Stanford Research Institute
Stanford Electronics Laboratories
Department of Electrical Engineering
Stanford University
Stanford, California 94305

SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

Syracuse Research Corporation
Center for Chemical Hazard Assessment
Merrill Lane
Syracuse, New York 13210

Tennessee Eastman Company
Laboratory of Industrial Medicine
P. O. Box 511
Kingsport, Tennessee 37662

Tohoku University, Dept of Chemical Engr
Sendai 980,Japan

Union Carbide Corporation
Chemicals and Plastics
Research and Development Department
P. O. Box 8361
South Charleston, West Virginia 25303

U. S. Army Environmental Hygiene Agency
Aberdeen Proving Ground
Maryland 21010

University of Minnesota
Department of Mechanical Engineering
Minneapolis, Minnesota 55455

University of North Carolina
Department of Environmental Sciences
and Engineering
School of Public Health
Chapel Hill, North Carolina 27514

APPENDIX B

RESULTS OF LITERATURE REVIEW

APPENDIX B

RESULTS OF LITERATURE REVIEW*

The review of information available for personal air monitors involved the evaluation of a variety of devices. Descriptive supplemental information abstracted for the body of the report is provided in this Appendix for

(1) Organic Vapor Sampling and Analysis --
Includes general information useful to evaluate potential application of studies for development of personal monitors for ambient air.

(2) Passive Monitors --
Detailed discussions are presented for devices commercially available and in the development phase.

(3) Active Monitors --
- active personal monitoring devices for organic compounds and pumps which may be adapted for this application

(4) Collection Devices --
Specific evaluations of adsorbent materials and impingers are described separately in this section since applications may be feasible for both passive and active personal monitors in ambient air.

(5) Miniature Gas Chromatograph --
This device is discussed separately in order to distinguish between the unit and other devices which are only microprocessor controlled.

Literature articles and personal communications are cited by number as listed in the alphabetically ordered bibliography (identical to the reference system used for the body of the report).

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* Accuracy, detection limits, interferences, and usefulness of devices and techniques are presented as stated by the respective authors. Verification of all claims pertaining to a specific device is the responsibility of the reader.

1. ORGANIC VAPOR SAMPLING AND ANALYSIS

A number of methods have been developed and evaluated for sampling and analysis of a specific organic compound or class of compounds. Applications of these methods to commercial development of passive and active personal monitors are described in the following sections of this Appendix. Both sorbents and impingers have been used for collection of organic vapors, however, charcoal tubes are most commonly employed. A variety of detection methods have been described, dictated predominantly by compound characteristics. Studies, grouped by target compound or compound class, are described below in alphabetical order for the following compounds:

Acrolein
Acrylates
Amines
Anilines
Benzidines
Carbon disulfide
Chlorinated isocyanuric acids
Cyclopentadiene
Diazomethane
Dinitrotoluene
Ethylene oxide
Furfural
Hydrazine
Hydrocarbons and Common Organic Solvents
Mercaptans
Methyl isocyanate
Nitrosoamines
Organic bases
Organic sulfates
Organometallics
Organophosphates
Phosgene
Propiolactone
Thiourea
Vinyl Chloride.

Acrolein

Ref. No.

30

A personal air sampling method, using activated carbon followed by analysis by gas chromatography, was developed by Hurley and Ketcham for acrolein in the 0.05 to 5 ppm range for a five-liter air sample. The sensitivity is 0.25 microgram of acrolein. Acrolein can be adsorbed on hydroquinone-treated carbon and desorbed with efficiencies approaching 90 percent using 1,2-dichloroethane. Columbia JXC and Barnebey-Cheney Type 580-26 carbons were the only carbons tested that showed collection and desorption efficiencies of acrolein in the 90 percent range. Samples must be analyzed the same day or frozen and analyzed within 5 days. Airborne contaminants such as propylene, acrylic acid, acetaldehyde, acetic acid, and isopropyl ether do not interfere in the chromatographic separation when using 9% (w/w) Carbowax 20 M-Terephthalic acid on 40/60 mesh Chromosorb T column. Acetone in amounts greater than 2 parts per million might interfere.

Technical Comments

Specially treated carbon adsorbent; GC analysis.

Acrylates

Ref. No.

Bosserman and Ketcham developed a method for air sampling and analysis of vapors of acrylate monomers. This method has been used for personnel monitoring, evaluation of exhaust ventilation, and for measuring area concentrations, all involving pilot-scale coating formulation and application. Concentrations as low as 0.05 parts per million by volume can be measured with the exception of 2-ethylhexyl acrylate which can be measured as low as 0.01 parts per million by volume. The acrylate monomer vapor is adsorbed on activated silica gel, desorbed in acetone, and analyzed by gas chromatography using FFAP or OV-17 liquid phase columns. Three statistical studies show this method is well within the accuracy and precision limits OSHA requires for methods of monitoring personnel exposure to air contaminants (± 25 percent). This method has been applied to the following acrylate monomers: 2-ethylhexyl acrylate, hydroxylethyl acrylate, isodecyl acrylate, methylcarbamoyloxyethyl acrylate, 2-phenoxyethyl acrylate, esterdiol-204-diacrylate, and esterdiol-204-4-ethoxydiacrylate. The retention times of isodecyl acrylate and hydroxyethyl acrylate overlap. 5

Technical Comments

Silica gel adsorbent; GC analysis.

Amines

Air samples were collected with sorbent tubes containing silica gel and the methylamine was stabilized by spiking the sorbent with hydrochloric acid. Samples were prepared for analysis by desorbing the methylamine from the sorbent with water. Desorption efficiency tests, performed on 300-mg portions of 45/60 mesh silica gel, indicated an average desorption efficiency of methylamine from the silica gel of 98.3 percent. Test atmospheres of methylamine in air at approximately 5 ppm, 10 ppm (OSHA standard), and 20 ppm were dynamically generated to test the method for sorbent capacity, storage stability of collected samples, and to assess precision and accuracy. 4

The sorbent tube capacity was evaluated by sampling dynamically generated methylamine test atmospheres at high humidity. The sorbent tube, containing 300 mg of silica gel, demonstrated a capacity in excess of 1.3 mg of methylamine when test atmospheres of 21 ppm methylamine and 83 percent relative humidity were sampled at 0.2 l/min. The precision and accuracy of the method was assessed by collecting samples of test atmospheres at three levels of known concentrations, and good precision was indicated by a coefficient of variation of 2.6 percent. The results for sorbent tube samples were within 10 percent of the results for independent samples taken by bubblers containing an acid solution. In a test for storage stability, the results of

samples analyzed immediately were within 1 percent of those analyzed after a 7-day storage period.

Ref. No. 4

A Model 14 ion chromatograph (Dionex Corp.) was used to analyze the methylamine as the methylammonium ion. Quantification of the methylammonium ion was accomplished by comparing experimental and standard peak heights. The detector response was shown to be linear from 3 to 90 µg/ml, with a detection limit of 1 µg/ml. For the recommended 24-liter collection volume, the lower limit of detection in the atmosphere was therefore 0.4 mg/m^3.

The silica gel - ion chromatographic method is applicable to other aliphatic amines since uncoated silica gel has been shown to be a suitable collecting medium for a variety of amines and the ion chromatographic method of analysis developed for methylamine has been demonstrated to be a very specific method for identifying and quantifying many lower aliphatic amines.

Technical Comments

Silica gel adsorbent; ion chromatography detection.

Anilines

Wood and Anderson developed a method for air sampling and laboratory analysis of vapors of six aniline compounds, namely, N,N-dimethylaniline, o-toluidine, 2,4-xylidine, p-anisidine, o-anisidine, and p-nitroaniline. Air is drawn by a personal sampling pump from a worker's breathing zone through a silica gel sampling tube. The silica gel section is transferred to a glass stoppered tube and desorbed with ethanol. An aliquot of this is analyzed chromatographically to determine the amount of each aniline compound present. The sampling tube can be used for short-term sampling at 1000 cubic centimeters per minute or for sampling up to 8 hours at 200 cubic centimeters per minute. Brief periods of elevated temperatures (50°C) or reduced pressures (to 500 mm mercury) do not affect the retention or recovery of aniline samples collected on silica gel. Long term (up to 1 month) storage effects of interest were migration and sample decomposition. If the analysis of the silica gel is to be delayed beyond 7 days after sampling, each tube should be filled with an inert gas and stored under refrigeration to reduce migration effects. 69

Technical Comments

Silica gel adsorbent, GC analysis.

Ref. No.

Campbell and Konzen conducted a study to measure aniline vapors in air using diffusion tubes. Tubes of 1.5, 3.0, and 4.5 cm lengths were tested under controlled conditions of relative humidity, air temperature, and vapor concentrations. The results indicate that the use of a passive diffusion dosimeter for determining time-weighted average concentrations of aniline is feasible. Upon analysis of the statistical and experimental data, it was concluded that the 3.0-cm dosimeter would give the most consistent determinations of the vapor concentration of aniline. Thus, a tube of 3.0 cm length and 1.05 cm inside diameter containing 150 mg of 40/60 mesh silica gel resulting in a diffusion path of 2.74 cm is the appropriate geometry for use as a passive aniline vapor sampling device. 9

Technical Comments
Diffusion tube evaluation using silica gel.

Benzidines

Investigators at Los Alamos Laboratories developed air-sampling and analytical procedures for benzidine, 3,3'-dichlorobenzidine and their salts. The sampler described will collect either physical form, aerosol or vapor, with high efficiency and should be applicable in all situations. It is small, employs no liquids and should be amenable to personal sampling with battery operated pumps. 44

The sampling chamber used in the laboratory allowed as many as ten samples to be collected simultaneously from a zone of homogeneous aerosol. Air is drawn through a glass-fiber filter followed by a bed of silica gel to collect the benzidine products as either particles or vapors. The compounds are extracted from the sampler and analyzed by high pressure liquid chromatography with sensitivities in the range of 3 micrograms per cubic meter for 48-liter air samples. The methods were evaluated in the laboratory with test aerosol atmospheres and found to be unaffected by temperature or humidity of the sampled environment. However, the analytical results suggest that samples containing benzidine or associated salts should be analyzed as quickly as possible and should be stored at temperatures $\leq$ 15°C until analysis can be completed.

Technical Comments
Silica gel, HPLC analysis.

Carbon disulfide

Ref. No.

Research reported by McCammon, et al., describes a method for sampling and analyzing air samples for carbon disulfide (CS_2). Test atmospheres of CS_2 were generated dynamically using the syringe injection methods, and the theoretical concentration verified by a liquid adsorbent, colorimetric method. The CS_2 was adsorbed on charcoal tubes, eluted with benzene, and quantified with a gas chromatograph equipped with a sulfur flame photometric detector. The results compared with the colorimetric analysis. The senstivity of this method is 1 µg on a charcoal tube. The charcoal tubes were also tested for breakthrough volumes, holding power vs time, and the effect of air transport and temperature cycles. 41

Technical Comments

Charcoal adsorbent; GC analysis.

Chlorinated isocyanuric acids

Patassis and Komensky developed a method for the analysis of air samples for sodium dichloroisocyanurate dihydrate (NADCC) and trichloroisocyanuric acid (TCCA). In this method, NADCC and TCAA are collected from air using polyvinyl chloride-copolymer membrane filters. Each filter is extracted with water and the extract is titrated against sodium thiosulfate solution using platinum electrodes and constant current potentiometry. The unknown concentration of the samples is determined using calibration curves. The detection limit for sodium dichloroisocyanurate dihydrate is 3.8 µg/sample and for trichloroisocyanuric acid is 2.2 µg/sample. 54

This method was field tested at a chlorine dry bleach plant. NADCC and TCCA were collected separately, eliminating problems with interference. The titration method will neither separate nor distinguish NADCC in the presence of TCCA or the reverse, thus, the identity of either compound, as well as the identities of any other interfering compounds in the workplace must be known. Personal exposures to both total and respirable particulates of NADCC and TCCA were determined. The total particulates were collected on a Gelman DM-5000 polyvinyl chloride copolymer membrane filter contained in a three-piece closed-face cassette. The respirable particulate fraction (<10 µm aerodynamic equivalent diameter) was collected on the same type filter contained in a two-piece cassette mounted in a cyclonic separator. The samplers were attached to the worker's shirt lapel at the breathing zone; air was pulled through the sampler by means of a personal sampling pump. Calibration curves in the range of 0.1 to 2 mg of NADCC or TCCA indicated good linearity ($r = 0.999$, minimum). A recovery study of NADCC from filters indicated that NADCC can be extracted with 99.1 percent efficiency and 3.6 percent precision. Experimental

results indicate that this method may also be used for compounds containing halogens in a positive oxidation state, such as hypochlorites and chloramines. Ref. No. 54

Technical Comments

Polyvinyl chloride-copolymer membrane; potentiometric analysis.

Cyclopentadiene

Fernandez and Smith developed a method for cyclopentadiene involving the collection of a 3-liter sample on a sorbent tube containing 100 mg maleic anhydride coated Chromosorb 104. The cyclopentadiene and maleic anhydride react via a Diels-Adler condensation to form stable adduct. This adduct is desorbed with ethyl acetate, and analyzed by GC. Desorption efficiency tests were performed by spiking aliquots of the maleic anhydride-cyclopentadiene adduct onto 100 mg of maleic anhydride coated Chromosorb 104. The amounts spiked represented the amounts of cyclopentadiene which would be collected in a 3-liter sample at atmospheric concentrations of 37.5, 75, and 150 ppm. Six samples at each level were prepared, and allowed to adsorb overnight. The spiked samples were desorbed in 10 ml of ethyl acetate, analyzed and compared to standards made by spiking the cyclopentadiene-maleic anhydride adduct directly into ethyl acetate. The desorption efficiencies of the adduct were 97 percent, 100.4 percent and 98.3 percent for 0.302, 0.605, and 1.201 mg cyclopentadiene, respectively. 18

Technical Comments

Chromosorb 104 adsorbent coated with maleic anhydride; GC analysis.

Diazomethane

Harris conducted a study to collect a highly reactive species, diazomethane, in air at concentrations in the range of the OSHA workplace standard (0.2 mg/m^3). The methodology involves in situ formation of a stable derivative, methyl octanoate, by use of a solid support, XAD-2, coated with octanoic acid. Subsequently, the ester is desorbed with carbon disulfide and analyzed using a gas chromatograph with a flame ionization detector. For validation of the sampling and analysis method, a procedure was devised for continuous generation of diazomethane at an appropriate rate. Generator concentration was verified by sampling with impingers containing benzoic acid in xylene and titration of excess benzoic acid. It was possible to generate a room temperature atmosphere of diazomethane in air over periods of up to 4 hours. The coefficient of variation for the total analytical and sampling method in the CH_2N_2 concentration range of 0.17 - 0.80 mg/m^3 was 0.084. This method has potential for application to other reactive species in air. 22

Technical Comments

Adsorbent was XAD-2 coated with octanoic acid for formation of derivative; analysis by gas chromatography.

Dinitrotoluene

Ref. No.

Dinitrotoluenes exist in six isomeric forms and are used primarily as intermediates in the manufacture of urethanes. Secondary industrial applications include the production of explosives and as intermediates in dyes. 29

Investigators at Allied Chemical described a method for trapping dinitrotoluene vapors in workplace air using silica gel solid sorbent sampling tubes. Subsequent analysis by GC is feasible for the concentration range of 10 to 300 µg of dinitrotoluene per ml of solvent. For a 50 liter air sample, a concentration as low as 0.1 mg/m^3 can be detected reliably. The occupational exposure limit for dinitrotoluene is 1.5 mg/m^3. During the period the Allied Chemical Company conducted this research, NIOSH developed a method for the determination of mixed vapor and particulate forms of the 2,4-isomers of dinitrotoluene using a filter cassette connected in series to a midget bubbler containing ethylene glycol with high pressure liquid chromatographic analysis.

Technical Comments

Silica gel adsorbent; GC analysis.

Ethylene oxide

A liquid impinger personal air sampling method for assessing individual worker exposure to ethylene oxide was developed by Romano and Rennes. The method is based on trapping ethylene oxide in dilute sulfuric acid where it is converted to ethylene glycol. The ethylene glycol is determined by GC using a glass column packed with 5% (w/w) Igepal CO-990 on Teflon-6. This column produces linear calibration curves and symmetrical peaks. The method has been shown to recover 94.2 percent ethylene oxide in the 1 to 8 ppm concentration range. The sampling technique is independent of flow, sample size, and presence of other organics. The impinger technique described produces chromatograms free from carbon disulfide impurities encountered with charcoal tubes. The disadvantages of impinger methods include: (1) inconvenience of liquid samples due to spillage loss during handling and shipping, and (2) loss of water during sampling may cause error introduced by changes in weight. 56

Technical Comments

Liquid impinger (H_2SO_4); GC analysis.

Ref. No.

Qazi and Ketcham investigated the use of Columbia JXC activated carbon for collection of ethylene oxide from air followed by desorption using carbon disulfide and GC analysis. The method has a lower detection limit of 0.004 µg per injection or 0.15 in a 10-liter air sample. No interference due to the possible presence of contaminants such as acetaldehyde, acrolein, ethanol, ethylene dichloride, ethylene glycol, formaldehyde, propionaldehyde, propylene oxide, vinyl acetate, vinyl chloride, and water was found with the determination of ethylene oxide. Statistical evaluation of the method from a round-robin interlaboratory study at 0.5 and 5.0 ppm levels showed an average recovery of 97 percent with precision (relative standard deviation) and systematic error of 3.76 and 2.9 percent, respectively. A round-robin interlaboratory study was conducted to evaluate the method. 55

Technical Comments

Activated charcoal adsorbent; GC analysis.

Furfural

Grubic, et al., developed a method for the sampling and analysis of furfural and acetaldehyde. The compounds are derivatized by drawing a known volume of air through a midget bubbler containing a buffered solution of Girard T reagent. The derivative is analyzed on a high pressure liquid chromagograph equipped with a variable wavelength detector. The average recovery of the analytical method for three sets of samples was 100.4 percent. Appropriate standards were used to prepare a calibration curve of peak area vs furfural concentrations, which was linear over the range studied. In collection efficiency tests, test atmospheres at twice the OSHA standard were sampled with midget bubblers connected in series. Each bubbler contained 15 ml of Girard T reagent solution. Collection efficiency was 99.6 percent. Collected samples were stable for at least a week. 21

Technical Comments

Impinger collection and derivatization; HPLC analysis.

Hydrazine

Hydrazine and 1,1-dimethylhydrazine were trapped on sulfuric-acid coated silica gel. Aqueous sample elutions were made and the derivatives prepared by addition of 2-furaldehyde in sodium acetate solution and measured by GC. The concentrations of hydrazines in the proximity of the worker's breathing zone were 0.23 to 11

4.61 ppm for hydrazine and 0.22 to 1.98 ppm for 1,1-dimethylhydrazine. Ref. No.

Technical Comments 11

Treated silica gel adsorbent; GC analysis.

Hydrocarbons and Common Organic Solvents

Methods based on solid sorbent sampling, solvent desorption, and GC determination were developed according to NIOSH guidelines for hexachlorobutadiene, hexachlorocyclopentadiene, and 1,2-dichloropropane by Dillon, et al.. Various adsorbents, solvents, and GC detectors were investigated to determine those most suitable for each compound. The developed methods include: (1) for hexachlorobutadiene: adsorption with Amberlite XAD-2, desorption with hexane, and determination by GC with electron capture detection; (2) for hexachlorocyclopentadiene: adsorption with Porapak T, desorption with hexane, and determination by GC/ECD; and (3) for 1,2-dichloropropane: adsorption with a petroleum charcoal, desorption with 15 percent (v/v) acetone in cyclohexane, and determination by GC with electrolytic conductivity detection. For hexachlorobutadiene, the bias from an independent method averages -7 percent and the pooled relative standard deviation (RSD) was 9 percent in the concentration range of 10 to 2000 $\mu g/m^3$; for hexachlorocyclopentadiene, the bias was +1 percent and the pooled RSD was 8 percent for 13 to 865 $\mu g/m^3$; and for 1,2-dichloropropane, the bias was -42 percent, and pooled RSD was 2 percent for 120 to 922 $\mu g/m^3$. The adsorbed compounds were stable for 7 days at 25°C. 15

Technical Comments

Hexachlorobutadiene, hexachlorocyclopentadiene, 1,2-dichloropropane: specific adsorbent for each compound; GC analysis.

Brown and Brown found that average concentrations of aliphatic hydrocarbons in a factory atmosphere may be estimated by adsorbing an air sample onto silica gel. Aliquots of the standard atmospheres were drawn through silica gel samplers (1.5 cm internal diameter tube, 18 cm long, and packed with 20 g dried silica gel) by means of a battery-operated sampling pump operated at 1 to 2 liters per minute. After sampling, the silica gel was removed from the sampling tube and adsorbed organics desorbed with 50 ml methanol. Aliquots were analyzed using Chromosorb 101 (80-100 mesh) or 10 percent Carbowax 400 on Chromosorb W (80-100 mesh) in conventional gas chromatographs with flame ionization detection. The sampling device may be used for sample collection in both background and breathing zone atmospheres. Under relatively dry conditions, the recovery of all chloroaliphatics except methylene chloride was close to 100 percent for up to 200 liters of air at a sampling rate of 2 liters per minute. The efficiency of sampling methylene chloride was 7

close to 100 percent only up to 100 liters sampled under these conditions. In general, high humidity reduces the volume of air that may be sampled at or near 100 percent recovery of organics, probably due to deactivation of the silica gel. Ref. No. 7

Technical Comments

Silica gel adsorbent; GC analysis.

Brooks and West have reported preliminary research findings for the first year of a 3-year EPA project initiated to develop a portable, miniature, adsorbent collection system for sampling and preconcentrating organics in general, and carcinogens and associated compounds (e.g. mutagens, precarcinogens, and cofactors), in particular, from ambient air. The purpose of such a system is to assess the exposure of individuals and/or small groups of individuals to these types of compounds in various environments. Inherent in the ability to assess exposures is not only the sampling capability, but also analytical confirmation. The determinative step in this project will be glass capillary gas chromatography/mass spectroscopy (GC-MS). 6

Progress reported for the first year described the selection of candidate sorbent materials; the selection of test compounds for sorbent evaluation; the evaluation of the sorbent materials in terms of capacity, desorption properties, and physical properties that relate the pressure drops and ultimate system design, and the selection of a three-sorbent system based on Tenax-GC, Porapak R, and Ambersorb. The selection of this three-sorbent system was based on the need to have a system that would be capable of sampling a broad range of organic compounds in terms of volatility and polarity and still be amenable to recovery processes, particularly thermal desorption. Other sorbents evaluated during this work were Porapak N and SKC activated coconut charcoal. The test compounds used to evaluate sorbent characteristics represent a broad range in volatility and polarity: n-butane, benzene, propylene oxide, benzyl chloride, acrylonitrile, phenol, isooctane, naphthalene, bis(2-chloroethyl) ether, 1,2,4-trichlorobenzene, ethylene glycol, m-nitroanisole, n-hexadecane, phenanthrene, hexachloro-1,3-butadiene, 4-bromo-phenyl ether, succinonitrile, and o-nitroaniline. Tapered glass tubes of specific dimensions were determined to be the best means of containing the sorbents and a basic sampling system was designed, which consisted of three sorbent-filled glass tubes in a series of parallel arrangement, followed by optional flow control/measurement equipment (needle valves and rotameters), and ending with a portable, battery-operated pump. This research effort included three major phases. The initial research phase involved a comprehensive review of available literature on the use of solid sorbent materials for sampling organic vapors. Knowledge obtained included: capacity/efficiency information, desorption techiques, sorbent characteristics, sorbent conditioning procedures, and possible experimental techniques for sorbent evaluation and sampling validation.

The second phase involved sorbent evaluation and the third phase requires the design of the portable miniature collection system prototype. The report concludes with analytical development in the design, construction, and installation of a special capillary inlet system to permit the thermal desorption of sampling tubes, preconcentration of the desorbed sample in a trap, and introduction of the sample into the glass capillary gas chromatograph for analysis. Ref. No. 6

Technical Comments

Analysis by GC-MS.

A three-component sorbent system was selected using Tenax GC, Porapak R, and Ambersorb.

Test compounds with broad range in volatility and polarity.

Literature review on solid adsorbents for sampling organic vapors.

Design of prototype collection system in progress.

Hertlein conducted a study for organics in the university laboratory environment following student inquiries regarding exposure. The studies were carried out in four laboratory classes simultaneously for 1 month. Small self-contained, battery-powered personnal sampling pumps were used to obtain integrated samples in the breathing zones of students throughout the entire laboratory period. Activated charcoal tubes were used to concentrate and collect as many as a dozen hydrocarbon vapors simultaneously. Desorption efficiencies were determined using carbon disulfide followed by analysis using a gas chromatograph and flame ionization detector. A stainless steel column 20-feet by 1/8-inch diameter with 20% (w/w) SP-2100 and 0.1% (w/w) Carbowax 1500 stationary phase on 100/200-mesh Supelcoport provided better resolution than other methods usually recommended for hydrocarbon solvent work. In other cases, a 6-foot by 1/8-inch diameter stainless steel column containing 100/200-mesh Porapak Q was utilized with excellent resolution and stability. Results were converted to 8-hour, time-weighted-average concentrations. Despite very low hood face velocities (less than 50 fpm), the airborne hydrocarbon concentrations were orders of magnitude below OSHA standards. 24

Technical Comments

Activiated charcoal adsorbent; GC analysis.

A gas chromatographic procedure was described by Langvardt and Melcher which is capable of measuring both polar and nonpolar organic solvents present simultaneously in the work environment at concentrations between 1/100 and 1 times the Threshold Limit Values (TLV). Airborne organics are collected on a single activated charcoal tube for periods of 3 to 6 hours and desorbed with a two-phase (water/carbon disulfide) desorption 36

mixture. Organic and aqueous phases are analyzed separately on the same gas chromatographic column packed with Oronite NIW on Carbopack B. Recoveries were determined for 15 common solvents. Most recoveries were greater than 90 percent with all coefficients of variation being less than ± 10 percent. Examples of field sampling are also presented. This procedure is generally applicable for monitoring complex mixtures of volatile organic compounds in air. Advantages include excellent recoveries for polar solvents such as acetone and ethanol, utilization of common analytical instrumentation under a single set of operating conditions and compatibility with personal monitoring methodology. Ref. No. 36

Technical Comments

Charcoal adsorbent and two-phase desorption mixture; GC analysis.

Heat Desorption

A method using adsorption of organics on Chromosorb 101 or charcoal followed by heat desorption onto a gas chromatography column was described. The Bendix Flasher was used to conduct the heat desorption process and a Tracor MT-220 GC was employed with flame ionization extraction. Increased selectivity was cited as probable if capillary columns were used. This method was the forerunner of current methods using glass capillary column GC coupled to mass spectrometry for measurement of organics in air. 50

Technical Comments

Collection of organics followed by heat desorption and GC analysis.

Porous polymer beads for concentration of organics in air was used to provide the option of thermal desorption for sample recovery. The packing material used was Tenax GC and Porapak N. The modification required for use of a Hewlett-Packard Model 5711 GC with flame ionization detection was described. 13

The major advantage of the procedure is high sensitivity resulting from collection of the entire sample. The use of GC/MS was cited for minimization of analytical interferences affecting identification of compounds.

Technical Comments

Collection of organics on Tenax GC and Porapak N followed by thermal desorption and GC or GC/MS analysis.

Ref. No.

Hill and Fraser conducted a study to determine the feasibility of developing a passive dosimeter for solvent vapors using conventional gas detector tubes. In comparison with organic vapor passive dosimeters that use an activated collection element, a detector tube dosimeter is relatively inexpensive with no costs for laboratory analyses, and can be interpreted in field studies. Disadvantages of a detector tube passive dosimeter include less accurate measurements than may be obtained with activated collection elements, and the possibility of erroneous measurements due to interferences. 27

Detector tubes for toluene were cut to produce a nominal 0.5 cm orifice above the indicator material, and exposed to known vapor concentrations. The time needed to reach a predetermined stain length by simple diffusion was measured. Calibration charts were prepared for time vs concentration for a 1-mm stain, as well as for various stain lengths. Tests were performed to determine the effect of increasing the orifice length and of diffusion through the glass wool plug. Each of these parameters resulted in less reliable concentration measurements than tubes of relatively shorter orifice length having no glass wool plug. Diffusion theory was used to develop theoretical calibration charts for comparison with experimental results. The use of detector tubes having an orifice length of 0.5 cm were shown to be feasible for use as passive dosimeters based on experimental results.

Technical Comments

Gas detector tubes.

Willis studied personal sampling of combustible gases and made predictions for future technological improvements. Personal monitors through radiotransmission may be linked to a central information terminal. If the individual's monitor goes into an alarm condition, a channel will be opened in the radio terminal and the variations in concentration of combustible gas may be monitored by the control room computer. Each employee wearing a personal monitor will be part of an overall network of continuous inputs being monitored on a roving basis. Willis feels that despite these technological achievements, explosive gas monitoring should not be expected to improve due to solid state sensor technology. This conclusion is attributed to the solid state sensor response spread (units of response as related to the lower flammability limits). For example, ethanol: 16.6; isobutane: 5.4; and methane: 0.25. 68

Technical Comments

Combustible gases; remote alarm sensor.

Mercaptans

Ref. No.

Nathans and Jeong developed an absorber tube method for sampling mercaptan concentrations in air and validated the method for methyl mercaptan (CH_3SH). The tubes are constructed by inserting two plugs of glass wool, weighing approximately 0.25 g each into a 5/16-inch glass tube, 5 inches long. The first plug is inserted about 1 inch from one end of the tube. This plug is wetted with 0.5 ml solution prepared by dissolving 50 g of mercuric acetate, free of mercurous salts, in about 400 ml of water, mixed with 25 ml glacial acetic acid and diluted to 1 liter. The solution is added through the long end of the tube. The second plug is inserted 1 inch into the long end of the tube and also wetted with 0.5 ml of the absorbing solution. The tubes are capped with parafilm until use. When in use, the direction of flow is such that the wetted ends of the plugs face the air flow. Atmospheres with known concentrations of methyl mercaptans were generated and sampled. 46

The pressure drop across 24 freshly prepared tubes was determined at a flow rate of 300 ml/minute. The range was 25.0 to 44.0 mm Hg. The mean was 36.7 $\pm$ 5.4 (1 σ) mm Hg. Conversely, the variation of the flow rate was determined at a constant pump setting, so that the flow rate of one tube used as a reference was 300 ml/minute. The range was 275 to 315 ml/minute. The mean was 292 $\pm$ 11 (1 σ) ml/minute. Thus, the coefficient of variation was 0.057. A coefficient of variation of 0.10 was determined for combined sampling and analysis with standard atmospheres of methyl mercaptan at the 0.5, 1.0, and 1.5 OSHA standard levels and with a general colorimetric procedure for mercaptans for the analysis. The average recovery was 95 percent or better. Since colorimetry was used for the analysis, the combined sampling and analysis method is not specific for methyl mercaptan. Current studies are aimed at making the method specific for individual mercaptans.

Technical Comments

Treated glass wool plug; colorimetric analysis.

Methyl isocyanate

A method dependent upon the production of an intensely fluorescent fluorophor was developed by Vincent and Ketcham. The sample is collected by adsorption on XAD-2 ion exchange resin. The concentration of methyl isocyanate is determined following desorption with a solution of fluorescamine (Fluram) in tetrahydrofuran by high-performance liquid charomatography using a multi-wavelength fluorescence detector. Use of the ion exchange adsorbent and the high-performance liquid chromatographic procedure results in detection of 238 ng/ml of methyl isocyanate. 65

Ref. No.

This detection is equivalent to measuring 0.01 ppm in a 15-liter air sample volume. The limit of detection with linearity was determined to be 4.76 µg/ml which is 0.02 ppm in a 180-liter air sample (6 hours). No significant effects of moisture upon sample retention were noted. A cupric chloride prefilter was used to eliminate the interference of monomethylamine and other amines. The XAD-2 resin retained 99 percent of the compound, indicating that the method has the required precision and accuracy to provide reliable measurements of exposure. Samples were stored under refrigeration for up to 2 weeks without appreciable loss of methyl isocyanate. 65

Technical Comments
XAD-2 adsorbent; HPLC measurement with fluorescence detector.

Nitrosamines

Issenberg and Sornson developed a monitoring method for nitrosamine compounds in air. Volatile nitrosamines, for example, nitrosodimethylamine, nitrosodiethylamine, and nitroso-pyrrolidine at concentrations of $1.3\text{-}3.5 \times 10^{-10}$ g/l in air were adsorbed on Chromosorb series 101-108 and Tenax-GC. Specific retention volumes were determined at 25 and 200°C (temperatures of collection and desorption). GC analysis with a Hall electrolytic conductivity detector was used for quantification. About 15 nanograms of nitrosodimethylamine produced full scale recorder deflection. 31

Technical Comments
Tenax-GC and Chromosorb 101-108 adsorbents; GC analysis.

Organic Bases

Wood and Nichols designed an all-purpose sampling tube for vapors of organic bases which could be used with commercially available personal sampling pumps. The pump may be worn on the worker's belt or carried in a pocket and the tube may be attached to clothing in the breathing zone. The tube developed contains three sections of 150 mg, 300 mg, and 600 mg of activated silica gel separated by glass spacers (12 mm long, 7 mm O.D.) in an 8 mm I.D. glass tube. A silica gel mesh size of 20/30 or 20/40 was used, rather than 42/60, to reduce the pressure drop, allowing sampling at flow rates up to 1 liter per minute. Adsorbent sections were enclosed by Teflon screens which are more inert to concentrated acid added for sample stabilization than 70

Ref. No.

stainless steel sections. The diameter of the smaller beds in the 8-mm I.D. tube is reduced to 6 mm by the thickness of Teflon rings enclosing them. Sampler range is increased by having the option of two differing amounts of silica gel in the primary adsorbing section. The third section is available as an additional backup section. In the case of sampling for hydrazine compounds, the two small sections are coated with 40 µl of concentrated sulfuric acid before sampling to prevent sample oxidation. Other amines are stabilized after sampling by adding 20 µl of concentrated hydrochloric acid to the small sections and 80 µl to the large section. The organic bases collected on the silica gel were desorbed with a 4:1 methanol-water acidified solution. The analytical method used was GC with flame ionization detection, however, adequate detectability proved to be a problem with several of the organic bases studied. A Schiff base derivative formed by reacting primary amino groups with an aromatic aldehyde improved chromatographic detection. 70

Technical Comments

Hydrazines and amines; activated silica gel adsorbent tube; GC analysis.

Organic Sulfates

Gelland and Bright developed a method for dimethyl and diethyl sulfate using silica gel. Desorption was performed with acetone followed by GC analysis using a flame photometric detector. The collection technique consisted of drawing a known volume of air through a large two-section, glass sampling tube containing 520 mg of 20/40 mesh silica gel in the front section and 260 mg in the rear section. The silica gel was transferred to a 2 ml vial and 2 ml of acetone added. Desorption efficiency was about 90 to 95 percent. The minimum detectable concentrations in solution for dimethyl sulfate and diethyl sulfate are 2 µg/ml and 5 µg/ml, respectively. The minimum detectable concentrations in the atmosphere, based on a 20-liter air sample are 0.04 ppm and 0.1 ppm, respectively. 19

Technical Comments

Dimethyl and diethyl sulfate; silica gel; GC analysis.

Organometallics

Houk and Beaulieu conducted a study to develop an optimal air sampling technique for Plictran^{R} miticide. Of special interest was the collection technique for a volatile component of the miticide mist during tree spraying operations and analysis for that component by flameless atomic absorption spectro- 28

Ref. No.

photometry (AAS). Information gained about sampling and analytical techniques for this organotin compound may be applied to organotins in general. Various filtration sampling methods were compared to a control method of impingement of organotin into concentrated nitric acid. Filtration consisted of combinations of two filter types; glass fiber filters coated with tetramine-dichlorocopper (II), and uncoated filters were used. The filters were ashed with 2:1 concentrated nitric acid/sulfuric acid, and the residue was dissolved in 3 percent hydrochloric acid. All samples were analyzed by graphite furnace AAS with manual injection of 5 µl samples. A calibration curve was obtained using serial dilutions of certified standard 1000 ppm inorganic tin in 7 percent hydrochloric acid. Dual filters including one coated, were more efficient collectors of the organotin than single filters or two uncoated filters. Ten ppb of organotin could be determined accurately with graphite furnace AAS. A dual filter system with a high surface area coating may be a suitable method for personal sampling of organotin compounds. 28

Technical Comments

Collection on glass and PVC filter combinations; flameless AA analysis.

Coker described a collection and analysis technique using Porapak Q for monitoring lead alkyl vapor in air. The lead alkyl vapor is collected using a stainless steel tube (1.3 mm O.D. x 8.9 cm), packed with 300 mg Porapak Q. Volumes of at least 10 liters of air were sampled without breakthrough losses, allowing 8-hour shift sampling using one tube and low flow rate (20 ml/min) from a personal sampling pump. Tubes were stored for at least 5 days without loss of sample. 10

The tubes were analyzed in 2 minutes by heat desorption directly into an atomic absorption spectrophotometer burner. The analysis is specific for lead alkyls and detection limits are about 0.01 x TLV for 10 liters of air.

Technical Comments

Porapak Q adsorbent; atomic absorption spectrophotometric analysis.

Organophosphates

Ref. No.

A method for collection and analysis of trace quantities of organophosphates was developed by Kaminski and Melcher. The compounds studied include o,o-dimethylphosphorochloridothioate, o,o-diethylphosphorochloroidothiate, and monoethylphosphorodichloroidothioate. XAD-2 resin, a porous polymer, which has been used to collect 2,4-D herbicides, was used to collect these reactive organo-thiophosphates. These compounds tend to hydrolyze rapidly; however, adsorption on the XAD-2 resin apparently stabilized the compounds since reproducible recoveries were obtained after 7 days of sample storage. Glass collection tubes (17 cm by 0.5 cm I.D.) packed with four sections of a 3 cm bed depth of XAD-2 resin were used. Each section of the adsorbent was separated by a silanized glass wool plug. A U-tube dynamic sampling apparatus was used in generation of recovery data. The collection time period was 4 hours for a flow of 200 ml per minute and 8 hours for a flow of 100 ml per minute. For sample analysis, each section of adsorbent in the collection tube was extracted with 10 ml of chilled ethyl ether/hexane mixture. The extraction solution for each section and that found in the U-tube was combined and analyzed using a Traco 550 GC equipped with a flame photometric detector specific for phosphorus. Detection limits for organothiophosphates ranged from 1 ng to 5 ng of material based on a 5:1 signal to noise ratio, which could be improved through electron filtering. The investigators observed that all components were collected on the first and second sections of the collection tube. It was recommended that field sampling tubes contain a front section of 6 cm x 0.5 cm and a back section of 3 cm x 0.5 cm with 10 ml desorption volumes. When the above study was undertaken, the proposed industrial hygiene guide for these organothiophosphates was 1 ppm. The exposure limit has been lowered to 0.1 ppm, which is detectable using this method. 33

Technical Comments

XAD-2 adsorbent; GC analysis with flame photometric detector.

Phosgene

Diller, et al., developed a personal monitoring method for phosgene using a strip of filter paper treated with 4-(4'nitrobenzyl)pyridine and N-phenylbenzylamine. One half of the paper strip is masked. Phosgene exposure produces a red stain, of intensity proportional to the exposure dose. The measurable doses range from 5 to 500 ppm-min. No staining of the detector paper indicates an inhaled dose less than 5 ppm-min and no suspected health effects. Slight staining corresponds to an inhaled dose approximately 5-50 ppm-min. Initial irritation of upper airways is possible if inhaled in high concentration 14

and symptomatic treatment may be necessary. Distinctive staining indicates an inhaled dose approximately 50-400 ppm-min, which damages lower airways. Heavy staining indicates an inhaled does is greater than 400 ppm-min, which is considered life threatening. A device based on this principle is available from MDA which provides for more accurate exposure measurement using an electro-optical reader.

Ref. No. 14

Technical Comments

Treated filter paper; colorimetric measurement; MDA gas badge principal.

β-propiolactone

The use of p-nitrobenzyl pyridine (p-NBP) and deoxyguanosine (dG) on cellulose thin-layer chromatography (TLC) strips provides a sensitive, simple and inexpensive method of personal monitoring for β-propiolactone (BPL) and other direct-acting carcinogens. The studies that led to the development of this personal monitor were described by Segal and Loewengart. The monitoring badge was prepared as follows: spots of an acetone solution containing p-NBP were applied to a cellulose TLC strip next to spots of an aqueous solution containing dG, and the cellulose TLC strip was inserted into a film-badge holder. BPL was dissolved in ethyl ether to establish a desired concentration, and in all experiments, the ethyl ether solution was transferred to an erlenmeyer flask by micropipet. The film-badge holder containing the cellulose TLC strip was suspended approximately halfway into the erlenmeyer flask attached to the cork stopper by copper wire. At the end of the desired time exposure to BPL vapors, the cellulose strip was examined under ultraviolet light for fluorescence of dG. The film-badge holder was suspended halfway into the TLC developing tank over ammonium hydroxide and examined for the development of the characteristic blue color indicating alkylation of p-NBP by BPL. Results showed that in each case, the sensitivity of the reaction is related to the length of exposure of the cellulose surface to the BPL vapors. For the reaction of BPL with p-NBP, the limits of detection are in the lower ppb range for exposures longer than 1 hour, and for exposures equal to or less than 1 hr, the detection limit is always less than 1 ppm. The detection limits of the reaction between BPL and dG are generally 10 to 100 times greater than the reaction with p-NBP. Maximum sensitivity was reaching by 4 hr of exposure with p-NBP, but not until 24 hr with dG. The intensity of the blue color produced by the reaction between BPL and p-NBP is proportional to the concentration of BPL. Other direct-acting alkylating carcinogens such as bis(chloromethyl)-ether, chloromethyl methyl ether, ethyleneimine, dimethylcarbamoyl chloride, diepoxybutane and glycidaldehyde were detected in the lower ppb range.

58

Technical Comments

Treated cellulose thin-layer chromatography strips; ultraviolet fluorescence detection.

Thiourea

Ref. No.

Patassis developed an air sampling method for tetramethylthiourea and ethylenethiourea using midget impingers containing 15 ml water. Ethylenethiourea may also be collected from air using PVC or cellulose ester membrane filters which are extracted with water. Pentacyanoamineferrate reagent is added to the filter-extract or to the impinger contents to form a colored coordination complex. The adsorbance of the solution is measured spectrophotometrically at 590 nm, using 5-cm quartz cells. Stability studies of the complexes indicate that the color is very stable for the first 3 hours (degradation of less than 2 percent). The unknown concentration of tetramethyl- or ethylenethiourea samples is determined from calibration curves. Excellent linearity was shown by calibration curves in the range of 15-150 µg. Recovery studies indicate that tetramethylthiourea cannot be extracted from the PVC filters with water or methanol. Recovery studies for ethylenethiourea from the PVC filters using water resulted in 98.6 percent efficiencies and 3.16 percent precision. Extraction efficiencies from the cellulose ester membrane filters were 97.7 percent with 3.63 percent precision. The method is also applicable for the analysis of other thiourea compounds. 53

Technical Comments

Midget impinger; colorimetric analysis.

Vinyl chloride

Nelms, Reiszner, and West developed a permeation sampling technique for vinyl chloride using activated charcoal as an adsorbent. The vinyl chloride permeates the dimethylsilicone membrane and is trapped on the activiated charcoal which is removed for subsequent determination by GC. The sampling device is a badge having dimensions of 41 mm by 48 mm and a thickness of 7 mm. It weighs less than 35 g and requires no source of power. The method is insensitive to temperature and humidity and the major common interference is ethylene dichloride. However, utilizing a carbon disulfide extraction procedure eliminates the interference by ethylene dichloride. The investigators claim that the method is ideally suited to personal monitoring programs required by OSHA regulations, because the analytical data represent a time-weighted average exposure and require no further data reduction. The response of the system to vinyl chloride was linear over the range 1 ppb - 50 ppm. At the limit of 1 ppb, precision above 0.1 ppm for an 8-hr sample was 5 percent for thermal desorption while the carbon disulfide procedure yielded a precision of about 5 percent at 0.5 ppm. 47

Technical Comments

Dimethyl silicone membrane with activated charcoal; GC analysis.

Ref. No.

West modified this personal monitor and conducted an extensive evaluation study. The badge consists of a hollowed out aluminum plate which serves as a reservoir for activated charcoal, a silicone permeable membrane for gas collection, and a front grid which protects the membrane from physical abuse. Collaborative studies by a number of laboratories confirmed the accuracy of these personal monitors utilizing gas permeation for sample collection and quantification. Data generated as time-weighted averages produced linear responses for 5 ppb to 50 ppm vinyl chloride. The monitors were unaffected by variations in environmental conditions. 67

Technical Comments

Field evaluation of vinyl chloride badge; prototype for MINI-MONITOR marketed by REAL.

West and co-workers have extended the application of permeable membrane/adsorbent collection to additional toxic compounds, including: alkyl lead - DMS membrane with silica gel; benzene - silicone polycarbonate with activated charcoal; hydrogen cyanide - DMS membrane with sodium hydroxide. While no environmental effects were observed for the vinyl chloride badge, these three applications are affected by temperature. 66

Technical Comments

Permeable membrane; alkyl lead, benzene, HCN.

Myers, et al., described a method for personal-breathing-zone sampling of vinyl chloride in ambient air that uses activated charcoal for collection followed by thermal elution onto a gas chromatograph. The furnace used to desorb the vinyl chloride was described in detail. The method has a standard deviation of 0.04 at the 1 ppm level and a limit of detection of 20 ppb or lower. The method can also be used to monitor other organic material with high sensitivity. The adsorption tubes are prepared by cutting 80-mm lengths of 5-mm O.D. glass tubing. Both ends were fire-polished with the inlet partly constricted. Glass wool was packed into the inlet tube to a length of about 5 mm. The tube was filled with 60-80 mesh activated charcoal (chromatographic grade) and the open end plugged with glass wool. The tubes were conditioned by heating at 300°C under a flow of 10 ml/min nitrogen for 10 minutes. After conditioning the tubes were immediately capped. The personal monitoring apparatus consists of a Mine Safety Appliances portablu pump 45

Ref. No.

Model G with a MSA multiple tube assembly. In actual use, the pump is clipped to the belt and the holder to the lapel of the individual under test. Four tubes are exposed simultaneously to allow for replicate determinations of the same sample. 45

To test the reproducibility of the method, a standard sample was prepared by mixing 50 microliters of vinyl chloride monomer with 50 liters of air in a Teflon bag. Thirteen replicate samples consisting of 1 liter each were taken through individual charcoal tubes from the bag. Analysis of these samples containing approximately 1 ppm vinyl chloride gave values ranging from 1.17 to 1.30 ppm vinyl chloride; standard deviation 0.037.

Although the method was developed specifically for vinyl chloride, the investigators state that the procedure is generally applicable to the determination of a large number of organic vapors including acrylic and methacrylic esters, benzene, chloroform, ethyl propionate, ethylene chloride, methanol, methyl cellosolve, methyl ethyl ketone, methylene chloride, naphtha, t-butanol, toluene, vinylidene chloride, and xylene.

Technical Comments

Activated charcoal adsorbent; GC analysis.

Lande published a literature review describing monitoring analysis procedures for vinyl chloride including methods for preparing standards for determining response curves and calibration measurement. Lande concluded that the lowest detection limits and most specific measurements are achieved by scrubbing atmospheric samples with activated charcoal, desorbing the vinyl chloride, followed by analysis using GC. NIOSH currently recommends collecting samples using tubes packed with 150 mg of coconut shell charcoal, desorbing with carbon disulfide, and analyzing by GC equipped with flame ionization detection (FID); the method is capable of detecting less than 1 ppm vinyl chloride and has an apparent recovery of about 90 percent. With thermal desorption techniques, the detection limit can be reduced to the ppb level with no loss of accuracy or precision. Some field methods, such as infrared analysis and conductivity measurement, are capable of detecting 1 ppm or lower but are subject to interferences by other contaminants, and could be useful for evaluating sources of vinyl chloride leaks and for continuous monitoring. Permeation tubes are superior to gravimetric or volumetric methods for generating atmospheres of known vinyl chloride concentrations. 35

Technical Comments

Most efficient adsorbent judged to be activated charcoal, GC analysis.

2. PASSIVE MONITORS

Passive personal monitors employ either diffusion or permeation as the controlling mode of operation. Devices which may be classified as passive are most commonly known by trade names since the majority of these systems are currently commercially available. The scientific background for some of the passive monitors was described in the previous section with commercialization information highlighted in the Comments. The units most extensively studied include the Walden GASBADGE available developed by Abcor and available from National Mine Service Company, and 3M's Model 3500 Organic Vapor Monitor. Both of these diffusion devices employ charcoal for collection of vapors. DuPont's PRO-TEK series (G-AA, G-BB) also use charcoal vapor collection (strips) controlled by diffusion. A phosgene dosimeter manufactured by MDA utilizes a proprietary tape diffusion collector. Monsanto is developing a passive dosimeter using Porapak N as a collection device for common multicomponent organic solvent vapors.

Dosimetry research conducted by P. W. West at Louisiana State University has led to the development of dosimeters employing permeable membranes. Badges for vinyl chloride and a variety of organic and inorganic vapors were products of West's research. A commercial version of the vinyl chloride badge, the MINI-MONITOR, is available from Real, Inc. A Poroplastic film membrane badge is being developed by Moleculon for a variety of compounds including chlorine, ammonia, nitrogen dioxide, and other gases.

A combination diffusion/membrane device, the Porton Sampler, was developed by the British Chemical Defense Establishment (BCDE). The sampler consists of a gas permeable membrane (silicone rubber or polypropylene) backed by a charcoal cloth disc and is suitable for measuring compounds covering a wide boiling point range.

Published reports describing these passive monitors are discussed below grouped according to tradename, primary function, or collector material in the following order:

- GASBADGE (Abcor)
- Model 3500 Organic Vapor Monitor (3M)
- PRO-TEK Badges (DuPont)
- GMD Phosgene Monitor (MDA)
- MINI-MONITOR (REAL, Inc.)
- Poroplastic Membrane (Moleculon)
- Porapak N (Monsanto)
- Porton Sampler (BCDE).

GASBADGE

Ref. No.

The GASBADGE was developed by Abcor and recently sold to National Mine Service Company. Several evaluation studies of this device have been published. Thompkins and Goldsmith described the badge and presented data illustrative of accuracy and precision achievable. 64

The Walden GASBADGE dosimeter consists of a removable protective cover designed to prevent contamination or exposure during shipment and/or storage. The badge front has an opening to allow diffusion of the contaminant into the device, a protective screen, a draft shield, an open grid to define diffusion geometry and to minimize internal mixing. The collection element is either activated charcoal or an appropriate substrate impregnated with a chemical medium specific for the contaminant of interest. The back of the device includes a spring clip allowing it to be conveniently affixed to the individual to be monitored. The dimensions of the dosimeter are 5.08 x 6.51 x 1.59 cm, with a total weight of 28.35 g. The operating principle is based upon Fick's first law of diffusion. Analysis of the collection element after exposure yields the time weighted average (TWA) exposure concentration. Promising results were obtained with sulfur dioxide and nitrogen dioxide. Data also indicate the applicability of the GASBADGE dosimeters to the monitoring of a wide variety of organic vapors as summarized below:

Compound	Actual Concentration in Sampled Air, ppm	Conc. Measured Using GASBADGE, ppm
methyl ethyl ketone	90.3	87.8 ± 4.2 (n = 4)
ethyl acetate	138.7	138.9 ± 7.1 (n = 3)
styrene	21.4	21.7 ± 0 (n = 2)
benzene	13.4	12.5 ± 2.7 (n = 4)
benzene	13.0	14.1 ± 2.2 (n = 4).

Comments

Badge description; precision and accuracy data given.

Silverstein conducted a validation study for use of the GASBADGE to monitor acrylonitrile. The results of the exposure of 33 badges to controlled concentrations of acrylonitrile are summarized as: 61

No. of Badges	Acrylonitrile Exposure Conc., ppm	GASBADGE Measurements Average, ppm	Range, ppm	Std. Dev.
16	8.9	8.67	6.43-9.65	1.28
7	19	19.1	15 - 22	1.28
10	0.74	0.75	0.60-0.88	0.03.

Ref. No.

Additionally, 18 badges were exposed side-by-side with charcoal tubes in the Dow Badische plants for 6 to 7 hours. Measured concentrations of acrylonitrile were 0.8-3.8 ppm, 2.14 average for charcoal tubes; 1.6 to 4.1, 2.73 average for the badges. The difference, using charcoal tube data as reference, ranged from -0.7 to +15, averaging +0.6 ppm. The side-by-side data were obtained when ambient temperature range was 64°F to 94°F, relative humidity 30 to 80 percent, and all possible interfering contaminants present at concentrations much less than 1 ppm. The acrylonitrile was 10 to 100 times higher in air concentrations than all other compounds. Desorption of acrylonitrole from the badges was maximized by using 4 ml of 2 percent acetone in carbon disulfide, five tests yielding 94 percent. The investigator concluded that both charcoal tubes and Abcor GASBADGES™ are acceptable for monitoring acrylonitrile, within the limits of ambient conditions and interferences specified. 61

Technical Comments

Evaluation of 33 badges for acrylonitrile.

The U.S. Army Environmental Hygiene Agency conducted validation studies for the GASBADGE for monitoring a variety of organic compounds. The charcoal tube method was used to generate comparative data. Applications of the sampler were demonstrated on various concentrations of benzene, methyl isobutyl ketone, isooctane, butyl acetate, methyl chloroform, trichloroethylene, butanol and solvent mixtures. Variables studied included the effects of temperature, charcoal lot, and air velocities. In addition, the occurrence of "breakthrough" and effect of time on sample stability, were investigated. 3

Since both the dosimeter and the charcoal tube separate organic vapor from sampled atmospheres by selectively adsorbing the vapor on charcoal, the two samplers were observed to have certain desirable and undesirable features in common. The desirable features include the following:

- the quantity of adsorbate is directly proportional to the ambient concentration
- adsorption/desorption efficiencies for most organic vapors are high and reproducible
- most mixtures can be sampled as efficiently as single vapor atmospheres
- adsorption/desorption efficiencies are relatively independent of charcoal lot and normal fluctuations in temperature.

Ref. No.

Undesirable features shared by the two samplers include the following: 3

- loading must exceed a certain minimum to be accurately quantified
- if loading exceeds a certain maximum, adsorption efficiencies drop off significantly
- if exposure time exceeds a certain maximum, vapor already adsorbed on the charcoal may be lost due to desorption by air and "breakthrough"
- adsorption/desorption efficiencies must be determined for each compound analyzed.

The contrasting features between the two samplers include the following:

1) The charcoal tube pumps require electrical power to be operated. The dosimeter requires no power.
2) The charcoal tube pumps must be routinely calibrated. The dosimeter requires no calibration.
3) Dosimeters weigh one ounce and require no sampling accessories. The charcoal tube assembly weighs approximately 840 g and includes a packed glass tube, approximately 1 m of plastic tubing, and a pump. Consequently, the dosimeter is less cumbersome than the charcoal tube assembly.
4) In order to preclude vapor losses, dosimeter pads must be stored and shipped in tightly capped vials (or their equivalent); charcoal tubes must be capped with end-caps (or their equivalent).
5) Dosimeters require a certain minimum atmospheric mixing to prevent concentration profiles from being established immediately outside of the draft shield; charcoal tubes do not.
6) Charcoal tubes are normally used for sampling periods of less than 1 hr; dosimeters for sampling periods of 2 to 6 hr.

The most reproducible dosimeter data were obtained when the dosimeter was isolated from organic vapors prior to sampling, charcoal pads were not overloaded, and the pads were put in tightly capped vials after sample collection was complete.

Technical Comments

Desirable features of GASBADGE and charcoal tube method; common deficiencies of both systems; comparison of both systems.

Evans and Horstman conducted desorption efficiency experiments for styrene using activated charcoal in conventional air sampling and with the Abcor GASBADGE. An amount of liquid styrene that was the equivalent of sampling four hours at a concentration of 29, 50, 100, or 150 ppm was injected onto each of five sets of badges. Vapor exposure took place at 30.5, 55.5, 105, and 150 ppm. Ref. No. 17

The precision of the passive dosimeters was comparable to that of the charcoal tubes when vapor dosed in a controlled atmosphere chamber. Vapor dosing of the Abcor GASBADGE created a desorption efficiency versus concentration curve separated by 5% at 30 ppm and converging at 100 ppm. Extrapolation of these results to sub-ppm monitoring should not be done without supportive data.

Technical Comments

Comparison of Abcor GASBADGE with charcoal tube desorption efficiencies.

Model 3500 Organic Vapor Monitor

The Model 3500 Organic Vapor Monitor developed by 3M consists of a round nylon body about 4.5 cm in diameter, and weighs about 12 g. A charcoal adsorbent pad is located inside the monitor, separated by spacers from a diffusion membrane. Contaminants enter the monitor by molecular diffusion and are adsorbed onto the charcoal pad. Desorption/GC are used for analysis. The procedure for monitoring and analyses using the monitor is as follows: (1) the monitoring assembly is attached in the worker's breathing zone for a measured interval of up to 8 hours; (2) exposure is terminated and the monitor is converted to an analytical device by interchanging one part; (3) a measured volume of eluent is added; and (4) gas chromatographic sample analysis is carried out by conventional means. 20

The time-weighted exposure level (TWA) is calculated using the following equations:

$$mg/m^3 = \frac{\text{Corrected weight on monitor (nanograms)}}{\text{Sampling rate } (cm^3/min) \times \text{sampling time (min)}}$$

$$ppm = \frac{mg}{m^3} \times \frac{22.4/\text{mole}}{\text{MW g/mole}} \times \frac{T°K}{273°K} \times \frac{760 \text{ mm Hg}}{p \text{ mm Hg}} \quad .$$

The corrected weight on the monitor is obtained from the sample analysis after corrections are made for blank samples and desorption efficiency. The sampling rate for each contaminant determined experimentally by 3M are published. Environmental sampling is controlled by binary diffusion such that the rate of sample collection is a function of ambient concentration. The

relationship between environmental contaminant concentration and the weight of material collected by the monitor may be expressed by

Ref. No. 20

$$M = D(A/L)Ct,$$

where: M is total mass of contaminant collected (ng)
D is molecular diffusion coefficient (cm^2/sec)
A is diffusion path area (cm^2)
L is diffusion path length (cm)
C is environmental contaminant concentration ($mg/m^3 = g/cm^3$)
t is sampling time (sec).

It is assumed that the contaminant concentration at the face of the monitor closely approximates the environmental concentration, the monitor wall effects are negligible, and the collection efficiency of the sorbent element is unity. In normal use, environmental concentration, C, is to be determined, mass collected, M, is determined via GC, and the monitoring time, t, is measured. Therefore, a value for the D(A/L) term is needed to solve the equation. Substitution of the appropriate units for D, A, and L reduces to cm^3/sec units which defines the sampling rate for the contaminant and shows the correspondence between diffusion-controlled monitors and conventional pump methods. The diffusion-controlled monitors do, in effect, sample the contaminants in air at a useful, calculable rate. the driving force for sampling is the concentration gradient between the collection face and the sorbent layer in the monitor. Monitor calibration data are provided by 3M Company for organic vapors of industrial hygiene importance, including selected ketones, amides, Freons, aldehydes and chlorinated aliphatic hydrocarbons. The items which are provided are: sampling rate (D(A/L) from equation); recovery coefficient; exposure limit; environmental effects; sample storage recommendations; concise equations for calculation of results. The OVM is not recommended to monitor carbon monoxide, ethylene oxide, formaldehyde, isocyanates, methane, ethane, propane, methyl alcohol, methyl chloride, and methyl,dimethyl-, and trimethyl-amines.

Technical Comments

Badge description; TWA exposure calculation; relationship between material collected on badge and ambient concentration; calibration data available from 3M.

Mazur, et al., examined the 3M model 3500 organic vapor monitor (OVM) for monitoring organic vapors in hospital operating rooms. The OVM 3500 was used to collect 2-bromo-2-chloro-1,1,1-trifluoroethane (Halothane) and 2-chloro-1,1,2-trifluoroethyl difluoromethyl ether (Enflurane) in standard air mixtures over the range of 0.2 to 10 ppm. Additionally, exposures to known concentrations were conducted for various lengths of time. A side-by-side comparison of charcoal tubes and passive dosimeter collection characteristics were made on known air mixtures and 40

samples collected in operating rooms. The material adsorbed on charcoal from dosimeters and charcoal tube was desorbed with carbon disulfide and quantified using gas chromatography. In general, sampling rates from the OVM were in good agreement with theoretical values, whereas results from the carbon tubes showed a slight positive bias. A total of 44 OVMs were tested for halothane, 250 OVMs were tested for halothane, and 250 OVMs were tested for enflurane at four concentration levels (0.5, 2, 5, and 10 ppm). An overall efficiency of 100.6 percent and relative standard deviation (RSD) of 5.6 percent was obtained for halothane, and 96.5 percent recovery and an RSD of 35 percent were observed for enflurane.

Ref. No. 40

Technical Comments

Examination of use of Model 3500 OVM for monitoring hospital operating rooms.

Stricoff and Summers collected a series of personal samples under field conditions to supplement passive dosimeter evaluations conducted by others in the laboratory. The GASBADGE developed by Abcor and 3M's Model 3500 OVM were used to study more than 100 pairs of side-by-side dosimeter/charcoal tube exposures. Results of this study indicate that, employing statistical tests, the null hypothesis that there is no difference between the passive sampler data and the pump-and-tube data cannot be refuted. However, scatter observed in low concentration environments raised the question regarding the validity of any single sample that might be used for compliance determination. This study provides further insight into the capabilities and limitations of passive dosimeters. 63

Technical Comments

Comparison of passive dosimeters (GASBADGE and Model 3500 OVM) and charcoal tubes.

Hickey and Bishop conducted a field comparison of 78 sets of charcoal tubes and 3M Model 3500 passive vapor monitors. This simultaneous sample collection was conducted for 22 organic chemicals as part of a survey of tire manufacturing facilities. The chemicals were detected over a dynamic range sufficient for linear regression analysis. Every chemical except n-pentane showed high concentration with the 3M Model 3500 passive monitor than the charcoal tubes. A slight negative y-intercept was observed for nearly all chemicals which may indicate a detection threshold or lack of sensitivity in the passive monitors at low concentrations. 25

Technical Comments

Seventy-eight pairs of 3M Model 3500 and charcoal tubes evaluated for 22 compounds; sub-ppm detection threshold suggested which would preclude ambient air applications.

Calvo and Zaebst conducted separate research programs to compare the responses obtained for the GASBADGE and the Model 3500 OVM. Calvo used a unique quasi-dynamic exposure system. The sampling devices were hung inside a 36 inch-long duct which acted as a wind tunnel. The duct was placed inside a 500-liter polypropylene tank. Mixing and constant air flow across the sampling devices was provided by a small fan attached to the duct in the sealed chamber. The test atmosphere was constantly monitored with an infrared spectrophotometer. All exposures were conducted for a period of 6 hours and analysis was performed using standard gas chromatographic procedures. Ref. No. 8

Initially, two solvents, trichloroethylene and perchloroethylene, were utilized separately to assess data obtained using the two different dosimeters. A second series of tests employed a combination of these solvents. Due to similarities in molecular weight, but differences in polarity and diffusion coefficients, competition for adsorption sites was observed. Calvo concluded the following: (1) for single solvent exposure to trichloroethylene or perchloroethylene, both types of passive personal samplers appear to be reliable indicators of concentration as evidenced by average collision coefficients; (2) one type of sampler seemed to be more precise in estimating single solvent exposure as shown by a smaller range of collection coefficients; and (3) response of the devices to mixtures of the two solvents does not seem altered unless overloading of the collection element is approached. At this point, competition between solvents for adsorption sites can occur, resulting in a decrease in collection efficiency.

Technical Comments

Comparison of GASBADGE and Model 3500 OVM.

Zaebst conducted comparison studies of both dosimeters and compared monitoring data from these devices with data generated using activated charcoal tubes. Comparative sampling of the two devices was performed for four industries under either single or multiple contaminant conditions. In each of the industrial hygiene studies, a series of paired, full-shift samples (charcoal tubes and one or both of the dosimeters) were collected and analyzed for the compounds of interest. Paired samples were collected to minimize any differences resulting from variable environmental levels. Both personal (breathing zone) and area samples were collected. 71

Statistical analyses of matched pair samples obtained under varying environmental conditions showed significant correlations between the charcoal tube method and the GASBADGE monitor when sampling for toluene in a mixed organic vapor environment, for styrene in the presence of acetone, and for perchloroethylene

where no other organic vapors were present. A significant correlation was also obtained between the charcoal tubes and the 3M monitor when sampling for toluene in a mixed organic vapor environment. Significant correlations were not obtained when sampling for carbon disulfide where no other organic vapors were present, or when sampling for acetone in the presence of styrene.

Ref. No. 71

Results of analysis by the paired sample t-test for each of the four significantly correlated comparisons indicated a systematic error when sampling for perchloroethylene when no other organic vapors were present, and for toluene in a mixed organic vapor environment. One of the possible sources of the bias might have been an error in the diffusion constant used in calculating dosimeter results, although a published empirically determined constant was used.

Technical Comments

Comparison of GASBADGE, Model 3500 OVM charcoal tube.

PRO-TEK Badges

The PRO-TEK organic vapor monitoring badges were developed by DuPont. The G-AA dosimeter may be used to determine the time-weighted average (TWA) concentration of organic vapor contaminants in the air. The organic vapors are collected through the mechanism of molecular diffusion and adsorption onto an activated carbon element. The badge is designed to be worn near the breathing zone of personnel exposed to potentially hazardous substances. After exposure, the badge is analyzed with gas chromatographic procedures similar to those outlined in NIOSH Physical and Chemical Analytical Method 127 for charcoal tubes. The badge contains two covers which should be removed during monitoring if low constant contaminant concentrations are suspected. If high contaminant levels are suspected, one badge cover may be left on the badge to reduce the sampling rate.

38

Commercially produced badges are made from an injection process using high density polyethylene. Each charcoal strip in the badges contains approximately 300 mg of coconut-based charcoal impregnated in an inert polymer. The badge can be used for sampling times ranging from 15 minutes to 16 hours. The sampling rate for each contaminant is obtained from diffusion coefficient data supplied by DuPont. The sampling range of the badge is 0.2 to 2000 ppm-hr for most organic vapors being measured. This range is realized since variable sampling rates of approximately 50 to 100 ml/min may be used depending on whether one or both covers are removed. The charcoal capacity is approximately 300 mg and the recommended desorbing volume is 1.0 ml.

After chromatographic analysis, the corrected weight of each contaminant on the charcoal strip is calculated by subtracting the contribution of the blank sample and dividing the result by the desorption efficiency determined for the contaminants being analyzed. The TWA user exposure is calculated using the following equations: Ref. No. 38

$$\frac{mg}{m^3} = \frac{\text{corrected weight on badge (ng)}}{\text{sampling rate } (cm^3/min) \times \text{sampling time (min)}} = \frac{\mu g}{cm^3}$$

$$ppm = \frac{mg}{m^3} \times \frac{22.4 \text{ l/mole}}{MW \text{ g/mole}} \times \frac{T°K}{273°K} \times \frac{760 \text{ mm Hg}}{p \text{ mm Hg}} .$$

Currently, a number of laboratories, including government, academic, and industrial facilities, are testing the PRO-TEK™ Organic Vapor G-AA Badge. The following suggestions were provided by DuPont for this testing:

- The badge has been calibrated to accurately measure between 35 and 400 ft/min face velocities when operating with both covers removed.
- The use of a wind tunnel is recommended to control face velocity effects.
- No more than 8 badges and charcoal tubes should be tested at one time with a minimum of 6 inches between each device.

Selection of the 100 ml/min or 50 ml/min sampling rate will depend on the ppm-hr exposure anticipated during the test, as illustrated in the following diagram:

		Expected Sampling Range (ppm-hr)		
		0.2-100	100-4000	Special Situations
Relative Humidity	< 90%	100*	50	50
	≥ 90%	50	50	50
Face Velocity (ft/min)	< 35	50	50	50
	≥ 35	100	50	50

* Units are ml/min.

The 50 ml/min sampling rate (one cover removed) should be used under the following conditions:

- Expected sampling range of 100-4000 ppm-hr exposure. This condition would exist in either long sampling times such as 24 hr or for measuring gases with high TLVs (i.e., up to 500 ppm for 8 hr).

- High relative humidities (i.e., >90% where breakthrough or saturation of the charcoal is suspected).
- Stagnant air conditions where face velocities of <35 ft/min are anticipated
- Special situations, as if poor adsorption or migration of the contaminant is anticipated during or after exposure.

Ref. No. 38

The 100 ml/min sampling rate (both covers removed) should be used when the expected sampling range will be 0.2-100 ppm-hr exposure and when relative humidities will be less than 90%, or when face velocity will be at least 35 ft/min. This sampling range would exist for either short sampling times such as 15 minutes or for measuring gases with low TLVs (i.e., less than 12.5 ppm for 8 hr).

Desorption efficiencies may be determined by using a phase equilibrium method in which known concentrations of contaminant in the desorbing solvent are added to the charcoal strip in a vial and allowed to equilibrate overnight. If no transfer occurs, the desorption efficiency is 100 percent. 16

Technical Comments

PRO-TEK G-AA; badge description; exposure calculation; manufacturer's recommendations for testing the PRO-TEK G-AA dosimeter; conditions for selection of 50 ml/min sampling rate and conditions for selection of 100 ml/min sampling rate.

The PRO-TEK^{TM} G-BB organic vapor badge with backup is a passive monitoring device used to determine the time-weighted average concentrations of organic vapors in the air. When analyzed, the backup section will indicate whether the capacity of the badge has been exceeded. The front section of the badge normally collects all of the contaminant. The backup section serves two purposes: (1) to indicate when saturation of the front section has occurred, and (2) to extend the total sampling time up to the point of saturation. The exposed charcoal collection strips are desorbed with 1.0-1.5 ml of desorbing solvent and analyzed chromatographically. The G-BB badge is designed to be worn near the breathing zone of personnel exposed to potentially hazardous substances. To activate it for use, remove the protective cover and clip badge to employees shirt collar. Each badge is individually numbered to facilitate accurate record keeping. The G-BB badge is recommended for use: (1) when sampling for compounds having a high vapor pressure such as vinyl chloride, methylene chloride, acetone, Freon^{R}, or pentane; (2) when the sampling is to be done in high relative humidity (>80%) or at high temperatures (>90°F); (3) for screening purposes. 38

Technical Comments

PRO-TEK G-BB dosimeter; recommended G-BB uses given.

Three of the commercially available (3M, DuPont, Abcor) diffusion based, personal monitors were evaluated for possible use for toxic organics in ambient air. Test compounds were benzene, chlorobenzene, and six chlorinated hydrocarbons. An in-series EC-PID GC method was used to quantify pollutants collected on the charcoal collectors and extracted with 5% carbon disulfide in methanol. Tests of detection limits, blank levels, and desorption efficiencies were performed. DuPont badges were less contaminated than the 3M devices which were less contaminated than the Abcor badges. Variable desorption efficiencies with DuPont badges of 16-81% were found with only those for chloroform, carbon tetrachloride, and 1,1,1-trichloroethane greater than 79%. Comparison of calculated lower useful limits for the DuPont device with ambient concentrations showed that only benzene, carbon tetrachloride, 1,1,1-trichloroethane, and trichloroethylene could be detected in a 24-hour sampling time. Improvements in blank levels and detection limits would allow the detection of all other tested compounds except 1,2-dichloroethane and chlorobenzene.

Ref. No.

12

Technical Comments

DuPont PRO-TEK, 3M Model 3500 OVM, and GASBADGE evaluation; blank levels measured.

Phosgene Monitor (MDA)

MDA has developed a gas monitoring dosimeter (GMD) for phosgene. The presence of phosgene is indicated by a dark red color that appears on the adsorbent. This reaction is an instantaneous, non-reversible chemical reaction and the color produced is proportional to the phosgene concentration. The dose level can be determined by comparing the intensity of the stain with a visual color comparison chart in ppm-minutes. More accurate readings can be obtained by using an electro-optical reader in ppm-minutes.

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Technical Comments

Technical basis described in previous section of this appendix (Reference 13).

MINI-MONITOR

Ref. No. 48

The MINI-MONITOR is comprised of a permeable membrane (dimethyl silicone) and an activated charcoal collector. This device is commercially available for monitoring air for vinyl chloride from REAL, Inc.

The Mini-Monitor employs permeation sampling, weighs 35 grams, has no moving parts, and requires no source of power. Sampling consists of placing activated charcoal in the monitor and clipping the monitor to the individual of interest. The charcoal is removed at the end of the desired sampling period and analyzed. Mini-Monitor operating conditions are:

- Linearity--The rate of collection of vinyl chloride is linear from 5 ppb to at least 50 ppm
- Detection Limit--0.02 ppm for an 8-hr sample (based on CS_2 extraction and GC-FID determination with a sensitivity of 0.5 ng)
- Effect of Temperature--Less than 5 percent from 0° to 40°C
- Effect of Humidity--Nil from 0 to 100 percent
- Interferences--No known interferences if analytical finish is free of interferences.

Application for monitoring Freon 12 and methyl chloride is under development.

Technical Comments

Vinyl chloride monitor; additional technical background in previous section (pp B-20-22); linearity and detection limit; future use for Freon and methyl chloride.

Poroplastic Membrane

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Moleculon is developing colorimetric passive dosimeters and sorbent tubes as liquid impinger replacements based upon ultramicroporous, homogeneous, membrane material called Poroplastic^R. Properties of Poroplastic film for these applications are:

- a transparent, high-liquid-content membrane containing approximately 90 percent liquid
- a highly retentive binding medium with pores of approximately 30 A
- an oleophilic matrix with broad reagent compatibility
- a physically strong film with a tough crystalline structure
- a very permeable medium which allows chemical reactions to take place at rates comparable to typical solutions.

The Poroplastic passive dosimeter, which is used both visually and instrumentally, incorporates a non-reversible color change. At present, the chlorine dosimeter is ready for marketing while the ammonia and nitrogen dioxide dosimeters are still in the developmental stages. Ref. No. 49

The badge will have five major components: sensitized Poroplastic film, a diffusion barrier, a transparent backing, a badge case, and a color chart. The wearer and/or supervisor will be alerted to the extent of exposure since the color change is easily observed on the front of the badge. The exposure level may also be quantitatively measured using a densitometer, an instrument more easily used than a spectrometer. The badge label will contain space for important record keeping: wearer name, date, exposure time, and exposure reading.

The Poroplastic Chlorine Badge has a color range of pale yellow to deep blue-purple. Since the TWA of chlorine is 1 ppm, these color changes occur over a range of 0 ppm-hr to 8 ppm-hr. The change in color is cumulative over the time and concentration of exposure.

Application for other gases are in various stages of development for sulfur dioxide, hydrogen sulfide, carbon monoxide, and formaldehyde. A breakthrough detection system is planned for direct incorporation using colorimetric techniques.

Technical Comments

Poroplastic membrane properties; composition of dosimeter; chlorine dosimeter; additional applications.

Porapak N

Two prototype passive dosimeters have been designed by Monsanto Research Corporation. Orofino and Usmani evaluated the dosimeters. The first dosimeter contained a Porapak N element and was used in some initial laboratory studies. Hexane was used as a standard to generate responses versus exposure time, sorbent capacity, humidity, levels of exposure concentration, and slopes of the response curves. A series of studies was conducted to determine proportionality, sensitivity, integrating capability, and adsorber retentivity. The use of benzene at the 1.2 ppm level gave quite satisfactory results, as did a mixture of 1.2 ppm benzene and 1.5 ppm acrylonitrile. The second dosimeter, an all plastic design, with provision for closure to activate and deactivate the collection of vapors, consisted of a dosimeter cover, two sections, 2-cm diameter disk shaped adsorbent element; and dosimeter case with element holder of 0.8 cm diameter aperture. After cleaning and baking, Porapak N (0.3 g) was loaded into the dosimeter in a clean environment free of any organic contaminants. 52

Excellent integrating capability with good linear response was obtained with an organic vapor containing 45.6 ppm hexane, 8.2 ppm vinyl acetate, 47.0 ppm toluene, and 9.3 vinylidene chloride. Response versus exposure time of the dosimeter to 1.5 ppm acrylonitrile with Porapak R again gave a linear proportional response despite background from the desorption of Porapak R.

Ref. No. 52

The investigators concluded that, with proper selection of adsorbent, excellent multicomponent organic vapor integrating capability and retentivity is provided for many organic vapors of interest. Responses of the dosimeters seemed quite predictable. The effects of varying the design ratio between the two dosimeters used was reflected in measured sensitivities and adsorbing capacities of the two devices.

Technical Comments

Benzene and acrylonitrile study; responses given for hexane, vinyl acetate, toluene, vinylidene chloride.

Porton Sampler

Bailey, et al., developed the Porton Diffusion Sampler available from the British Chemical Defense Establishment. The sampler consists of a gas permeable plastic membrane backed by a charcoal cloth adsorbing disc mounted in a plastic holder similar to the familiar radiation film badge. Diffusion of vapors through the membrane into the charcoal cloth is directly proportional to the external vapor concentration. After exposure for a known time, the adsorbed material is eluted from the disc and airborne contaminant can be measured by chromatographic and spectroscopic methods. Two membranes were found to be very satisfactory: a thin silicone rubber membrane and a porous polypropylene film. The charcoal cloth is a very efficient non-specific adsorbent for organic materials with boiling points at or above room temperature but adsorbents which are specific for certain gases can be devised.

1

The investigators demonstrated the utility of the device by measuring atmospheric levels of carbon tetrachloride, styrene, Freon 12, and methyl ethyl ketone, compounds covering a boiling point range from -30°C to +145°C. The range of substances which the Porton Sampler can use probably is limited (1) by substances of very low volatility which are firmly held by activated charcoal, and (2) by substances of very high volatility which may be so weakly retained on the adsorbent that they cannot displace water, carbon dioxide, and other gases already adsorbed on the charcoal. Many of the features of the Porton sampler are found in permeation-type samplers developed in this country.

Technical Comments

Permeable membrane backed by charcoal disc; silicone rubber and polypropylene both suitable; applications for carbon tetrachloride, Freon 12, methyl ethyl ketone.

3. ACTIVE MONITORS

The active personal monitors commercially available include a variety of pumps and associated collection tubes for organic vapor collection and analysis. **Normally, systems have not been designed for the collection of a specific compound.** In the majority of cases, trade names of the devices have not been proposed (such as Gasbadge, Organic Vapor Monitor) or widely adopted with the exception of the Accuhaler and Chronotox systems marketed by MDA. In addition, a larger number of devices are commercially available. Therefore the detailed descriptions of these devices will be presented here in alphabetical order according to manufacturer with tradename, if any, added. The units described in order of presentation of discussion include:

- Bendix Corporation
  - BDX55 HD
  - BDX34LF
  - BDX102
  - BDX60
- Daco Products, Incorporated
  - P0301 and P0304
  - Diff Sampler
- DuPont
- Environmental Measurements Pulse Pump III
- Matheson Gas Products Unico Model 400
- MDA Scientific, Incorporated
  - Accuhaler
  - 4000 Miniature Continuous Monitor
  - Chronotox
- Mine Safety Appliance Company Model C-210
- National Draeger, Incorporated Polymeter
- Sipin Company, Incorporated
  - SP15
  - Sipin-Kitawaga Dosimeter

Bendix Corporation

Bendix Corporation has developed active and passive personal monitoring systems for organic and inorganic contaminants including a series of BDX pumps, charcoal tubes, midget impingers, open ended filter holders, respirable mass samplers, reagents for colorimetric determination of contaminants, and a gas detector system (direct reading detector tubes and a piston-type volumetric pump). The detector system compares favorably with tubes/pumps available from National Draeger, MSA, and Matheson-Kitawaga. These tube/pump systems have been developed for detection purposes and not personal monitors, however, application to personal monitoring in the workplace and ambient air monitoring is feasible.

BDX55 HD Personal Monitoring Pump. This pump is used in sampling for coke oven emissions, gases and vapors with impingers for 9 hr, dusts using 0.8 and 0.45 micron pore size, high resistance filters for a minimum of 8 hr.

Features are:

1. Flow range 1-3 ℓpm
2. Flow capacity 2 ℓpm at 20" water pressure across collecting media
3. Flow accuracy ±5% between 3" and 10" water back pressure
4. 12 hours sampling through 37 mm 0.8 micron filters
5. Flow rate: Consistency of ±5% of initial setting with (2) adjustments during sampling period
6. Dimensions (cm): 11.9 × 12.7 × 6.5
7. Weight: 850 g
8. Estimated Price: $400

Technical Comments

Description and specifications for BDX55 HD.

BDX34LF Sampler. This pump is recommended for monitoring organic vapors using a BDX 88 and standard charcoal.

Features are:

1. Flow range 25 ml-200 ml/min

2. Can be used to sample for a minimum of 8 hr with long-term detector tubes at flows as low as 20 ml/min
3. Dimensions (cm): 11.9 × 10.2 × 6.5
4. Weight: 620 g
5. Price: $410

Technical Comments
Description and specifications for DBX34LF.

BDX102 Personal Monitoring System. This system is used for dusts, and vapors, e.g., acetone, benzene, carbon tetrachloride, chloroform, methylbutyl ketone, toluene, trichloroethylene and vinyl chloride. The BDX44 was adapted for a low flow rate by exchanging the flow regulator and the flow meter.

The battery pack provides full shift sampling of 8 to 10 hr in either flow range (25-200 ml/min or 1 to 3 l/min). High flow rates against high voltage resistance are accomplished using an optional higher voltage battery pack. The unit measures 31.8 × 28.6 × 11.4 cm and weighs 2150 grams.

Technical Comments
Description and specifications for BDX102.

BDX60 Super Sampler Constant Flow Pump. This pump is equipped with an electronic feedback loop to maintain flow control accuracy and used for continuous sampling of vapors, hazardous gases, and particulate matter.

Features are:

1. Operating temperature range 0°C to 40°C
2. Flow range 1-3 ℓ/min
3. Accuracy ±5% of flow setting
4. Restricted flow indication dual mode (selection switch)
5. Power requirement. Self contained 6 vdc rechargeable Ni-Cd battery pack.
6. Equipped with precision diameter orifice to selectively collect dusts, vapors, and gases down to 1 micron. Orifice diameter is precisely ±0.1 mm.
7. Dimensions (cm): 11.9 × 12.7 × 6.5
8. Weight: 840 g
9. Price: $400

Technical Comments
Description and specifications for BDX60 Super Sampler.

Daco Products, Incorporated

Daco's sample pumps are designated to sample through impingers and charcoal tubes to give a flow variation not to exceed 10 percent over 8 hours.

Operating conditions and specifications include:

1. Adjustable Flow Rate. Voltage to the motor may be varied to control motor speed (flow) and the pressure/volume regulator may also be adjusted for low flows. The pressure/volume regulator permits bypassing of much of the flow, while maintaining higher motor speeds and a more uniform flow rate with reduced pulsation. Batteries may be placed in series for higher flow rates.

2. Double diode protection of the motor will stop the flow of current should any part of the circuit be shorted.

3. Power Supply. "D" cells may be removed from the case for charging thus permitting the pump to be used continuously. Nickel-cadmium or lead acid batteries are available and energizer batteries may also be used.

4. Sampling Time. Using 200 ma as an average current drain, sampling time will vary from approximately 5 hours for Ni-Cd batteries to over 20 hours for lead acid batteries.

5. Operating Temperature. Most batteries will operate at low temperatures. Ni-Cd batteries are useful to about 0°F, however, below 0°F, the lead acid battery must be used.

6. Dimensions (cm): 7.0 × 12.4 × 3.8

7. Weight: 200 g with Ni-Cd and 530 g with 2 lead acid batteries.

8. Cost:

   (1) P0301. Sample pump with 2 Ni-Cd batteries and charger. $85.00

   (2) P0304. Sample pump with 3 lead acid batteries $160.00

Technical Comments
Description and specifications for P0301 and P0304 pumps.

Ref. No.

The Diff Sampler available from Daco uses liquids to collect toxic substances. Concentration may be measured either colormetrically or with a Daco conductivity meter. The Diff Sampler contains a well in the top, instead of wire screens. In the bottom of the well is an inert wick which extends into the sampler, or tube. Liquid detecting solution is placed in the well and the cap is placed on the tube. Detecting solution saturates the wick on which the toxicant is absorbed. When the test is finished, additional collecting solution is added to the tube to remove the adsorbed toxicant. The solution which has changed color is then compared with color standards for conversion into ppm. The conductivity measure technique is more sensitive and can be used for both spot sampling and time weighted average. A major disadvantage of conductivity measurement is lack of specificity. That is, if more than one substance is present, the relative conductivity of the contaminant must be checked. The Diff Sampler is battery operated and small (pocket size); the probe is small enough to fit into passive samplers. Daco has also developed a spill-proof impinger with replicable cell parts. The impinger may be rotated 360° and tipped as much as 80° with no liquid spill.

Technical Comments
Diff Sampler with liquid collection and colorimetric or conductivity measurement; spill proof impinger.

DuPont

Sampling of vapors and particulates require accurate determination of the volume of air sampled. The accuracy of the sample volume measurement is as important as the accuracy of the analytical technique. NIOSH criterion for a valid sampling method is that 95 percent of the samples come within ±25 percent of the value. In this criterion, the coefficient of variation of pump error is assumed to be 5 percent and the calibration of the pump is unbiased. With many pumps, as particulates accumulate on the sampling head, resistance to flow increases causing the flow rate to decrease thus inducing a systematic error in the volume measurement. Pumps equipped with a rotameter must be regularly checked during sampling. DuPont pumps, after calibration with a primary standard such as a bubble meter, maintain constant flow with an electronic flow sensing and feedback flow control mechanism which automatically adjusts the pump drive signal to maintain the preselected calibrated flow rate. The flow rate setting is independent of the collection device pressure drop. A variety of collection devices from solid sorbent tubes (such as

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charcoal tubes), long-term detector tubes, liquid impingers, cyclones and particulate filters with pressure drops of up to 10-25 inches of water column can be used while maintaining a ±5 percent flow rate accuracy. Pump flow rates from 10-4000 ml/min can be used depending on the type of pump selected.

Ref. No.
2

Technical Comments

Description and specifications for DuPont pump model numbers P30A, P125A, P200A, P2500, and P4000.

Environmental Measurements, Incorporated

The Pulse Pump III marketed for $145 is recommended for use as a personal sampling pump and an ambient air collector. Applications include hydrocarbons, sulfur hexafluoride, radon, and carbon monoxide. The Model 11-1900 pump measures 4 x 7.3 x 10 cm and weighs 225 g with batteries.

Technical Comments

Description and specifications for Pulse Pump III.

Matheson Gas Products

Matheson markets a precision hand pump, Unico Model 400 for the collection of 100 ml of sample for detector tubes. Each tube is specific for the detection of a particular substance. Detector tubes are available for many volatile organics. Matheson's pump kit which includes the pump, metal carrying case to accommodate six boxes of detector tubes, spare parts, photograph of the micro orifice and operating instructions costs $90. Detector tubes containing 10 tubes per package cost about $10 per package.

Technical Comments

Description and specifications for Unico Model 400.

MDA Scientific, Incorporated

Sampling pumps such as the early MSA Model G are inadequate for low flow rate. The second generation pumps such as the Sipon Model SP-1 and the DuPont Model P125 were developed to handle low flow rates; however, measurement of flow rate was not sufficiently accurate. Moore et al describe the Accuhaler pump operating principles designed to provide accurate low total volume. The Accuhaler is a controlled inhalation system which samples at rates from 5 to 100 ml/min. The most important feature is that the Accuhaler uniquely carries out a total volume measurement with no dependency on

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on techniques such as mechanical displacement and measurement of flow rate. Moore et al noted a deficiency in information available for charcoal tube sampling during the course of the development of the Accuhaler pump. A wall chart was prepared available from MDA Scientific summarizing expected range, recommended sampling rate, maximum tube load, desorption efficiency and eluent for 120 organic compounds.

Ref. No.

43

Technical Comments

Development and operation of Accuhaler pumps described. User's guide for charcoal tube sampling available from MDA Scientific.

The Accuhaler pump marketed by MDA operates by repetitive, reproducible, controlled inhalations into a chamber of defined volume through a limiting orifice. The volume of gas sampled is metered. Accuhaler is designed for use with a wide range of collection techniques including charcoal tubes, silica gel, length-of-stain chemical tubes, and other adsorbents.

Accuhaler Specifications:

Sampling Rate Ranges: Model 808: 0.5-100 ml/min
Model 818: 1- 25 ml/min

Standard Limiting Orifices: (Nominal Sampling Rates)
Set A: 10, 20, 50, 100 ml/min
Set B: 1/2, 1, 2, 5 ml/min
Set C: 2, 5, 10, 20 ml/min (Model 818 only)
Other orifices are available by special order.

Total Volume Readout: 5 Digit Mechanical Counter. Specially marked wheel for functional checking.

Volume Per Stroke: Approximately 4 ml. (Precise volume/count factor stated on instrument.)

Running Time: Rechargeable Models: Minimum 8 hrs between charges.
Disposable Battery Models: Minimum 8 hrs at 50 ml/min, 40 hrs at 10 ml/min.

Dimensions (cm): 14 × 6.4 × 3.2

Weight (g): 390

The Accuhaler costs from $330-430 depending on the number of orifices selected and batteries provided.

Technical Comments

Description and specifications for Accuhaler.

MDA developed the Model 4000 Miniature Continuous Monitor (MCM) designed to be worn in the person's breathing zone or placed at a work station. The pump aspirates air through a moving chemically impregnated tape producing a stain with intensity proportional to concentration of contaminant of interest. An integrating reader/recorder is available (Model 4100) which provides time average quantification data. Phosgene may be monitored from 0-0.4 ppm and toluene diisocyanate is measurable from 0-0.08 ppm. The tape moves at 2 cm/hr and the air sampling rate is 100 ml/min. The pump weighs 680 g and measures 15.2 × 5.7 × 10.2 cm.

Ref. No.

Technical Comments

Description and specifications for Model 4000 MCM.

A microprocessor-controlled personal monitoring system is also manufactured by MDA. The Chronotox provides hard copy data for personal alarm conditions, chemical concentration versus time 90 second data points and 8 hour threshold limit value or 15 minute and 8 hour threshold limit value. When programmed permissible levels are exceeded, the Chronotox records the duration of the event, and how far the permissible levels were exceeded. The Chronotox™ also gives information on possible causes of excessive concentration and corrective action to be taken. The Chronotox System can be expanded by the addition of a Personal Tape Sampler (PTS) to the sensors that are being employed. The PTS is a universal monitor which accepts any one of the 12 different chemically impregnated tapes. The PTS Sampling Head is about the size of a cigarette pack and includes the appropriate chemcassette of impregnated paper, a tape advance mechanism, and the optical system for tape readout. Available PTS cassettes include impregnated tape for: organic isocyanates, dinitrotoluene, hydrogen chloride ammonia, toluene diamine, and aromatic amines.

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Data display, sensor output, and data output are provided by the Model 4102 Chronotox microprocessor. The concentration of toxic materials being measured by the sensor is updated every second or every 90 seconds. In addition, a sensor output has the capability of storing up to 5 response curves. If additional sensors are used, a simple exchange of programmable, read-only memories provides monitoring capability for 5 more sensors. The Chronotox microprocessor data can be read either by the Datagram® readout or the Digital Readout Unit. The 4102 stores an average concentration value in memory every 90 seconds. Using the Datagram® Readout format, the 480 data points accumulated every 12 hours are transcribed to produce an accurate profile of concentration levels versus time. In addition, an 8 hour time-weighted average (TWA) value is recorded. When read with the Digital Unit, the 4102 generates a battery voltage reading, four 15 minute TWA values for each hour of exposure, including the elapsed time notation, and an 8 hour TWA value.

The price of the Chronotox equipment is:

Ref. No. 34

• Personal Tape Sample	$1250
• Microprocessor	2000
• Readout and XY Recorder	5150
• Small Digital Readout	990
• Tapes (each)	15

Technical Comments

Description and specifications for Chronotox.

Mine Safety Appliance (MSA) Company

The Model C-210 pump available from MSA is designed primarily as a personal sampling pump. The pump is powered by a rechargeable 2.4 V nickel-cadmium battery pack with a normal life of approximately 600 operating hours. Sampling period after each charge is 10 hours nominal at 200 ml/min and 2 inches H_2O. MSA provides accessory equipment including sample collection tubes and holders; charcoal and silica gel (organic vapor aromatic amines); and colorimetric tubes for detecting carbon dioxide, carbon monoxide and hydrogen cyanide.

Technical Comments

Description and specifications for Model C-210 pump.

National Draeger, Incorporated

The combination of a personal monitoring pump and a specific detector tube provides a system for determination of average concentration of toxic gases or vapors a worker is exposed to during a shift. Based on a series of chemical reactions that produce color changes, Draeger developed substances which are suited specifically for long-duration measurement. The Draeger Polymeter is a peristaltic pump with a calibrated silicone hose which has a constant flow rate in the range of 15 cm^3/min. The pump draws about 900 cm^3 of air per hour through the connected tube. The indicating layer of the tube changes color - the length of the colored portion of tube indicating the amount of exposure. The cost of the Polymeter is $700 and the quantification system costs an additional $1390. Battery chargers retail for $110.

Technical Comments

Description and specifications for the polymeter.

Sipin Company

Sipin developed a personal sampler under NIOSH sponsorship. The Sipin Model SP-15 continuously draws air samples from a worker's breathing zone, through a sorbent tube for the duration of a working shift, and measures the total volume of air that has been pumped. At present, tubes of standard NIOSH activated charcoal are used as sorbents. New sorbents compatible with the SP-15 and similar pumps are being developed by Sipin. Features include a 2-200 ml/min flow rate, linear calibration, overload alarm, and pocket size (3.2 × 6.4 × 13 cm; 310 g). The SP-15 Personal Sampler Pump is carried in the pocket of the worker or clipped to a belt and connected to a charcoal tube holder containing standard NIOSH activated charcoal. Applications reported for the Sipin SP-15 include personal monitoring of organic solvents in establishments for degreasing of heavy machinery, plastics and rubber processors, chemical plants and refineries, pharmaceutical industries, paint manufacturers and paint shops, metal treating and plating shops, dry cleaning establishments, textile plants, pulp and paper plants, vinyl chloride and polyvinyl chloride manufacturers and users.

Technical Comments

Description and specifications for the SP-15.

Sipin also has available the Sipin-Kitawaga personal Multiple Gas Dosimeter System which uses Sipin Personal Sampler Pumps and Sipin-Kitawaga length-of-stain Gas Dosimeter Tube to monitor the air actually breathed by the worker. The Gas Dosimeter Tube is carried in a protective holder that can be fastened to the worker's clothing so that the sample is taken directly from the individual's breathing zone. The pump draws the air at the time-weighted average concentration of the toxic gas for periods up to and exceeding 8 hours. An accurate reading can be obtained and compared with allowable limits. Sipin's dual gas adapter permits samples to be drawn through two dosimeter tubes simultaneously by a single pump. This permits simultaneous measurement of time-weighted-average concentration of two different gases. Adapters for simultaneous monitoring of more than two gases are available.

Technical Comments

Description and specs for the Sipin-Kitawaga multiple gas dosimeters.

4. COLLECTION MEDIA

Several studies were conducted to evaluate impingers or adsorbents as collection devices. These articles are summarized.

Impinger

Ref. No.

Heitbrink and Doemeny developed a modified impinger as an improvement over the standard midget impinger for industrial hygiene air sampling including personal sampling. However, the modified impinger still contains several shortcomings, including shape and pressure loss. The investigators conclude that these shortcomings might be eliminated through slight modifications in a manufacturing process. The development of a plastic, non-breakable impinger, or a plastic-protected glass impinger is suggested. Some of these modifications are found in Daco's spill-proof impinger described earlier (page B-43). However, the Daco impinger does not meet NIOSH and OSAA method specifications that midget impingers must be compatible with bubbler stem. 23

Adsorbents

Parameters which affect long term eight hour air sampling using a tube containing solid sorbent were described by Melcher et al. The various procedural steps to be followed were cited with emphasis on the sampling procedure. The complexities of the gas chromatographic techniques commonly employed for detection of specific compounds were not treated. The criteria examined included sensitivity, specificity, reproducibility of analysis of applicable concentration, reproducibility of apparatus, adaptability, simplicity, and capability for automation. Specific factors treated included guidelines for breakthrough and effect of compound properties on collection efficiencies. Type of sorbent, size of collection tube, flow rate, humidity, temperature, and migration affect breakthrough. A number of factors influence recovery efficiencies: temperature, humidity, coadsorption of other compounds, desorption time, and loss during storage play significant roles in this process. General criteria for a validated method for sampling air with solid sorbents were developed and include: 42

1. Accuracy and precision of combined analytical and collection procedures for 1/10 TLV to 2 TLV: ± 16% relative at the 95% confidence level.
2. Total recovery efficiency of $\geq$ 75%.
3. Bias between total recovery and desorption efficiency less than ± 10% relative.

Ref. No.

4. Capable of taking 10-15 minute samples at ceiling and excursion levels. 42
5. Minimum sampling time one hour, preferred 4 to 8 hours for time weighted average.
6. Stored samples compare to initial samples within ± 10% relative after 14 days.
7. Flow rate of the sampling pump known with ± 5% accuracy.

Quality assurance procedures for field sampling are discussed and the importance of communications before, during, and after the event is cited.

Technical Comments
Designation of specific guidelines for validated air sampling method for solid sorbents.

Hirayama and Ikeda evaluated the applicability of activated carbon felt for use with Abcor's GASBADGE for monitoring exposure to mixed vapors or organic solvents. A mixture of n-hexane, ethyl acetate, and toluene in a 1:4:1 ratio was the solvent system studied. Seven preparations of activated carbon felt tested were cut into oblong pieces of 3.0 cm x 4.5 cm and housed in GASBADGE™. Four Dynamic flow type vapor exposure chambers (60 cm x 60 cm x 60 cm), arranged in parallel, were employed. Most of the seven carbon felt preparations tested failed to absorb n-hexane in humid air or the amounts absorbed were not proportional to vapor concentrations in dry air. When the sum of the three vapor concentrations was greater than three times the workroom threshold limits, two preparations showed capacity to absorb n-hexane even in air with relative humidity of 95 percent. Furthermore, the amounts adsorbed during 4-hr exposures were linearly related to the vapor concentration of at least 4.5 times workroom threshold limits when the three vapor concentrations were added. At lower concentrations, the absorbed amounts were proportional to the exposure duration of up to 8 hr. Short term peak exposure could also be de ected; the ratio between the observed and the expected concentration was about 80 percent. 26

Technical Comments
Carbon felt used with GASBADGE.

Sever and Story evaluated several adsorbents for analysis of vinyl chloride, vinylidene chloride, and methyl chloride. 59

Ref. No.

One specific coconut carbon, Pittsburgh PCB 12 x 30 Activated Carbon, was found to be the most suitable of the commercially available carbons tested for personnel sampling of vinyl chloride and related compounds. One gram of this carbon packed in a stainless steel tube (14 cm x 0.25" O.D. x 0.028" wall) can be used satisfactorily to collect vinyl chloride, vinylidene chloride, and methyl chloride according to the sampling conditions described. The study developed improved techniques of desorbing the carbon using carbon disulfide at dry ice temperature. Analysis is performed by GC with flame ionization detection. A variety of columns, for example, 20 percent DC 200 on Chromosorb W 80/100 mesh, Carbowax 4000 on Supelcoport 80/100 mesh, Porapak QA 80/100 mesh; Carbowax 4000 and Freon 12 on Porapak Q5, may be used for analysis. 59

Technical Comments

Coconut carbon most suitable for vinyl chloride.

Shou-Yien Ho conducted a study to determine the variation and stability of vinyl chloride collected on charcoal tubes as well as the accuracy and precision of the laboratory analytical results. The collaborative study involved 42 laboratories. Each laboratory analyzed duplicate sets of charcoal tubes containing vinyl chloride at two concentration levels. The variance analysis shows that the replication errors varied from 0.85 percent ot 1.43 percent. Sample variation (generation error) varied from 2.48 percent to 4.45 percent. The interlaboratory system error varied from 14.8 to 18.6 percent. The investigator concludes that the collaborative test shows that the permeation method is adequate to generate accurate, uniform, and stable vinyl chloride reference samples. It can be used to evaluate instrument performance. 60

Technical Comments

Charcoal tube comparison for vinyl chloride.

The effects of humidity, sample stability, sample migration, and variations in the desorption efficiency for charcoal tube air sampling are described. The variations between batches of charcoal indicated the need for a charcoal tube certification standard. Removal efficiencies differed by as much as 20% for n-butanol, 2-ethoxyethyl acetate and 2-butanone. 57

Technical Comments

Desorption efficiency for charcoal.

Samples of seven single component solvents which included benzene, carbon tetrachloride, chloroform, dioxane, ethylene dichloride, trichloroethylene, and xylene along with two solvent mixtures (benzene-xylene and ethylene dichloride-trichloroethylene) were tested in two phases by 15 laboratories. The estimated errors were: relative total error 12.72; analytical error, 9.49; and sampling error, 8.01. The data indicate that pump error is the major source of error in sampling.

Ref. No. 37

Technical Comments

Interlaboratory comparison with seven solvents and two mixtures using charcoal.

5. MINIATURE GAS CHROMATOGRAPH

Stanford Electronics Laboratory developed a prototype gas analysis system using a miniature gas chromatograph. Application of the miniature GC to ambient air monitoring is unlikely even when development is complete. Further improvements necessary for detection of organic compounds at ambient concentrations (50-200 parts per trillion) would require substitution of the thermal conductivity detector with a more sensitive detector. The use of capillary columns for improvement of separation of mixtures is also necessary. 32